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RESEARCH REPORT No. CX-31

Excitation of Molecular Vibration by Collision

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Abstract

We have calculated the cross section for excitation of the first vibrational level in the collision of two hydrogen molecules in the ground state. A perturbation scheme must be used because of the many-body problem involved. The cross section is calculated by a partial wave analysis. We consider the collision of two H_2 molecules because the intermolecular potential is reasonably well known for this case.

Because of the large masses of the particles, the de Broglie wavelength of the system is much smaller than the range of the intermolecular potential. Consequently many values of the angular momentum must be considered. We find that the major contribution to the total cross section comes from large values of the angular momentum - ℓ of the order of 10 to 20 - and that values of angular momentum up to about 80 must be considered. In order to solve the Schrödinger equation for arbitrary values of angular momentum with a Morse potential form for the intermolecular potential, the high speed computer Univac was used.

In the energy range of interest, 0.5 to 2 ev, the total cross section is obtained. At energies greater than 5 ev the values for the cross section are larger than the maximum permissible if particle flux is to be conserved, that is, our perturbation scheme breaks down at these high energies. However, the cross section for energies greater than 5 ev is not too significant since electronic transitions, which we have neglected, become appreciable.

We find the value of the cross section to be very sensitive to the precise values of the potentials used. This result is to be expected since the classical turning points of the motion occur at values of internuclear separation for which the potentials are steeply varying functions of nuclear separation. Consequently the calculation of an inelastic scattering cross section for most molecular systems - for which the details of the intermolecular potential are not known - must be considered approximate, at best.

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1. Review of previous work

1.1 Description of problem

1.1.1 Introduction

The characteristic collision processes in a molecular gas in the temperature range from 100 °K to 5000 °K are elastic scattering, and inelastic scattering which involves changes in vibrational and rotational quantum numbers only. Electronic transitions during collision will take place to a significant extent only at much higher temperatures, $E \geq 5$ ev (corresponding to 60,000 °K).

For most molecules, the spacing of the rotational energy levels is small (of the order of .05 ev), so that changes in internal rotational states on collision are very likely at room temperature (300 °K corresponds to .03 ev).

We are concerned, however, with the excitation of vibrational energy states on collision. The spacing of the vibrational states is of the order 0.1 to 0.3 ev for most molecules.* Since the inelastic scattering cross section near the threshold depends exponentially^[1] on the energy transferred from translational to vibrational degrees of freedom, the cross section will be very small near the threshold energy and increase rapidly with energy above threshold.

At temperatures below 5000 °K, electronic transitions do not occur to any appreciable extent, and so the Born-Oppenheimer^[2] approximation is very good. In this approximation the nuclei of the molecules are assumed to move so much more slowly than the orbital electrons that the collision is 'adiabatic' in the sense that the electrons have time to adjust themselves without transitions to the change in potential energy during the collision. The nuclei 'see' only the average field produced by the motion of the electrons. The Born-Oppenheimer approximation is good

* e.g., for N_2 , the spacing is 0.29 ev, for O_2 , 0.2 ev. For hydrogen, which is of course somewhat special, the energy difference between the ground and the first excited states is 0.54 ev.

so long as the nuclei do not have sufficient energy to induce electronic transitions. The intermolecular potential can then be defined as a function of nuclear separation only. The potential energy at each value of internuclear separation is calculated assuming stationary electronic motion.

Inelastic collision cross sections are needed to calculate rates of chemical reactions and of vibrational relaxation. The latter mechanism explains the dispersion of high frequency sound in di- and polyatomic gases. The inelastic scattering cross section is also needed in the calculation of three-body recombination coefficients [3], and the accommodation coefficient of a gas [1].

1.12 Formulation

Call the first molecule AB, the second C. The second molecule is considered to be a simple particle of appropriate mass. The motion of the center of mass is eliminated from the Schrödinger equation for the system by using the following coordinates:

$$\begin{aligned}
 (1) \quad \vec{\rho} &= \vec{r}_{AB} \\
 \vec{r} &= \vec{r}_C - (M_A \vec{r}_A + M_B \vec{r}_B) / (M_A + M_B) \\
 \vec{R} &= (M_A \vec{r}_A + M_B \vec{r}_B + M_C \vec{r}_C) / (M_A + M_B + M_C)
 \end{aligned}$$

These coordinates are shown in Figure 1. Here, $\vec{\rho}$ is the internuclear separation of the molecule AB and describes the internal vibrational motion; $\vec{r}$ is the distance

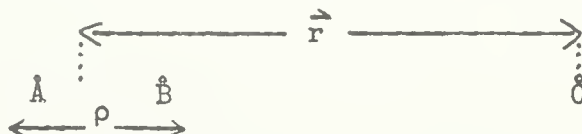


Figure 1

from the second molecule C to the center of mass of AB. This describes the relative translational motion of AB and C. $\vec{R}$ is the coordinate of the center of mass of the system as a whole and need not be considered explicitly.

The reduced masses then are

$$(2) \quad M_i = M_A M_B / M_A + M_B \quad M_e = M_C (M_A + M_B) / M_A + M_B + M_C \quad .$$

The coordinates (1) are particularly suited to the present problem. It is easily shown that the kinetic energy of the whole system reduces to a sum of squares in this coordinate system [4]. This is true whether the kinetic energy be calculated classically or quantum mechanically.

There are now two major difficulties in the formulation of the collision problem for inelastic scattering: (a) since we are dealing with a many-body problem, some suitable perturbation scheme must be devised; and (b) an approximation to the intermolecular potential must be found. The perturbation scheme we use consists in separating the intermolecular potential into two parts: an unperturbed part V^0 which is additive in the two coordinates $\vec{\rho}$ and $\vec{r}$, and a perturbation V' which couples the internal (vibrational) and external (translational) coordinates and thus induces the transition. The perturbation potential is assumed to be much smaller than V^0 . Thus we write

$$(3) \quad V = V^0 + V'$$

$$(4) \quad V^0 = V_i^0(\vec{\rho}) + V_e^0(\vec{r})$$

$$(5) \quad V' = V'(\vec{\rho}, \vec{r}) \quad .$$

Here V_i^0 is the internal potential energy of the molecule AB, and V_e^0 is the external (translational) potential energy between the two molecules. V' is the perturbation potential. It is clear that this perturbation approach will be valid only so long as V' is actually much smaller than V_e^0 . This will be true only if the molecules do not approach each other too closely during the collision. This condition is violated at high energies, and then the perturbation scheme breaks down. This result is discussed in Section 2.

The intermolecular potential V_e^0 is not well known quantitatively except for the simplest system, such as H_2-H_2 . For this reason some approximation to the intermolecular potential must be made. The general features of the intermolecular potential are well known. At large values of $\vec{r}$ the potential is essentially the attractive van der Waal's potential which varies as r^{-6} . At small distances the Coulombic repulsion of the electrons is dominant and there is a steep repulsive barrier. At intermediate distances an exponential form [5] will be more correct than a power series. Although the general features are well known, it is not possible to calculate analytically the intermolecular potential for any but the simplest systems. The angular dependence of the intermolecular potential has been calculated for H_2-H_2 , but not for any more complicated molecular systems. Because of these difficulties, one attempts to fit a spherically symmetrical potential with two or more adjustable parameters to available data on the molecular system. This work will be discussed in Section 1.3.

The major mathematical difficulty arises in the solution of the Schrödinger equation for even the simplest form for the intermolecular potential. The radial equation will involve the centrifugal potential term $\hbar^2 l(l+1)/2M_e r^2$ and is consequently intractable for even simple forms for the potential V_e^0 . Because of the large masses of the particles and the relatively long-range potential, many values of angular momentum l must be considered, and this considerably complicates the calculation. It is usual to perform the calculation only for the case $l = 0$, but past work has shown the inadequacy of this approximation [6]. This is further borne out in the present work.

1.2 Previous calculations of inelastic cross sections

1.21 Work of Zener, Jackson and Mott.

An important paper on the excitation of molecular vibration by collision was written by C. Zener^[7]. The techniques developed there for approximating the complicated many-body problem have been the starting point of most later calculations.

Zener approximates the intermolecular potential by the exponential form e^{-ax} . This is the asymptotic form of the resonance energy between two symmetrical diatomic molecules where x is the separation between the centers of gravity of the two molecules. This is of course a highly simplified form for the intermolecular potential which ignores the attractive part of the potential. At the energies of interest, however, it is a sufficiently good approximation and moreover is relatively tractable mathematically.

Only collinear collisions can be considered since not even the simple exponential approximation to the intermolecular potential yields a Schrödinger radial equation that is soluble for arbitrary angular momentum l . This approximation has been used by many writers since Zener although it is easily shown that for most systems of interest, many values of l will contribute to the inelastic cross section.

A brief consideration of the problem from the viewpoint of classical mechanics gives the following qualitative picture of the collision: when the time of collision is greater than the period of oscillation of the molecule, the collision will be 'adiabatic.' That is, the colliding atom or molecule will tend to act only on the center of gravity of the struck molecule, and hence the probability of a transition to an excited vibrational state will be small. Zener calculates the ratio of the time of collision to the period of vibration using a simplified potential and classical mechanics. The result shows that for most systems this ratio is large, and thus we can expect a small inelastic cross section.

These considerations suggest the use of a perturbation scheme to calculate the probability of transition to an excited vibrational state. An approximation to the exponential potential is used in order to solve the radial equation for $l = 0$ in terms of simple functions. Zener calculates the probability of deactivation of N_2 from the first excited vibrational state to the ground state on collision with He at room temperature. The result is $6 \cdot 10^{-8}$.

Jackson and Mott^[1] perform a calculation very similar to that of Zener's and apply the results to the calculation of the accommodation coefficient of a gas. The calculation proceeds in exactly the same way and gives the same result for the transition probability. However, the authors are able to solve the radial equation for $l = 0$ with a simple exponential form for the intermolecular potential, in terms of Bessel functions of imaginary order. This makes it possible to write down the transition probability in terms of simple functions for this choice of potential.

Devonshire^[8] and Zener^[9] carried out a slightly different calculation which takes into account the attractive part of the intermolecular potential. They were able to calculate the transition probability for an intermolecular Morse potential of the form

$$(6) \quad V = -D \left[2 e^{-(r-b)/2a} - e^{-(r-b)/a} \right] .$$

This potential is zero at $r = b - 2a(\ln 2)$ and has a minimum at $r = b$. It is physically more realistic than a single exponential even though it does not behave correctly for large r . At large r we expect the potential to go to zero as r^{-6} . The result obtained with this potential does reduce to that of Jackson and Mott in the limit D approaching zero.

Because the radial equation can not be solved in closed form for the potential (6) even for $l = 0$, a semi-classical method must be used in order to obtain the transition matrix element of the perturbation potential. This method

agrees with a quantum mechanical result only in the limit of high energies. We shall see in Section 3, however, that at these high energies the $\ell = 0$ approximation gives an incorrect result for the inelastic scattering cross section.

1.22 Work of K. Takayanagi

The next advance in the work of Zener was undertaken by K. Takayanagi^[10]. The higher angular momenta are taken into account by the approximation

$$\tilde{k} = \left[k^2 - \ell(\ell + 1)/\bar{R}^2 \right]^{1/2}$$

where $\bar{R}$ is some suitable value of r near the classical turning point of the motion. One then replaces k in the radial equation by $\tilde{k}$ and has only an s-wave radial equation to solve. The transition probability may then be calculated from the result of Jackson and Mott. For ℓ not too large, the gradient of $\ell(\ell + 1)/r^2$ is small compared with the gradient of the potential Ae^{-Br} , at least near the classical turning point. In this case the inclusion of the slowly varying $\ell(\ell + 1)/r^2$ term in the wave number k may represent some reasonable approximation to the behavior of the radial equation for different (small) ℓ .

K. Takayanagi and S. Kaneko^[11] have applied this method to the vibrational deactivation of O_2 by He. For large ℓ , of course, this approximation is unreasonable. However, the authors claim that the major contribution to the cross section comes from small ℓ values. In the transition probability calculated by Jackson and Mott the main factor is the term $e^{-a(K_f - K_o)}$. This term does decrease with increasing ℓ .

1.23 Work of Widom and S.H. Bauer

Widom and S.H. Bauer^[2] have investigated the vibrational deactivation of CO_2 on collision with H_2O using the semi-classical method developed by Zener^[9]. The method is extended so that the transition probability for vibrational deactivation

tion can be calculated as a function of impact parameter, the classical analogue of the quantum mechanical angular momentum. A spherically symmetric potential must be used in order to solve the classical equations of motion for the inter-nuclear distance as a function of time. This solution is then used to calculate the transition probability as a function of impact parameter at various energies. The transition probability decreases with increasing impact parameter, as expected. Also, many values of impact parameter give a significant contribution to the transition probability. The final result is quite sensitive to the precise values of the parameters in the unperturbed Lennard-Jones 12-6 potential and those in the perturbation potential. Widom and S.H. Bauer find that small variations in these parameters result in a large variation in the inelastic scattering cross section. This sensitivity of the inelastic cross section to the precise values of the potentials has been observed in the present work (Section 3).

1.24 Work of E. Bauer

Recently E. Bauer^[6] has attempted to take into account in a physically reasonable way the high order angular momenta which contribute significantly to the cross section. The number of angular momenta ℓ that contribute significantly to the cross section is given approximately by kd where k is the wave number and d the range of the potential. Since k is relatively large for a molecule because of the large mass, this will be a number of the order 10-100. Since it is a hopeless task to integrate the radial equation for many values of angular momentum ℓ , the problem is reformulated using an impact parameter b , rather than the angular momentum ℓ . The problem of summing over ℓ is thus reduced to an integration over b . The wave functions are obtained by the WKB method.

The method of impact parameter is well suited to problems of this type. Because of the large mass of the particles, the deBroglie wavelength is much smaller than the range of the intermolecular potential. Consequently one can speak of a

well-defined orbit for the collision. This means the WKB approximation for the wave functions will be a good approximation. On the other hand, it can be shown that a completely classical treatment is inadequate. Assuming that the coupling between the internal coordinate $\vec{p}$ and the external coordinate $\vec{r}$ is induced by a perturbation potential V' , one can calculate roughly the average momentum transferred in a collision. Then it turns out that $\delta p \delta x < \hbar$ for most values of the energy that are of interest. Hence a quantum mechanical treatment is called for. The combination of the WKB method for the wave functions and the impact parameter formulation instead of partial wave analysis is suited to the classical and quantum mechanical features of the problem.

The case of an H_2-H_2 collision is treated because there exist rather detailed calculations of the intermolecular potential for this system^[13]. Ultimately the matrix element of the perturbation potential between the initial and final states must be calculated. Since both the initial and final states are highly oscillatory functions, this integration is not easy to carry out. Approximations must be made in order to estimate the matrix element. An effective range of interaction is defined which includes the turning points of the orbit. The potential is then taken to be zero outside the limits of integration, which now extend only over the effective range of interaction, and is replaced by an average value within these limits. The precise numerical value of the effective range is unclear, yet the integral must be a very sensitive function of it. These approximations leave the numerical values of the calculation in doubt.

1.3 Experimental work on intermolecular potentials

1.31 Gas kinetic and other experimental data

Much work has been done in recent years in fitting a potential to a given molecular system. Two or more adjustable parameters are varied so as to obtain the best fit with available data. Most work has been done with a central potential, since there are not enough data on angular variation of properties of molecular systems.

Two potential forms have been exhaustively investigated: the Lennard-Jones 6-12

$$(7) \quad V = \lambda r^{-6} - \mu r^{-12} = -4\epsilon \left[\left(\frac{r_0}{r} \right)^6 - \left(\frac{r_0}{r} \right)^{12} \right]$$

and the exponential-six

$$(8) \quad V = \frac{\epsilon}{1 - \frac{6}{\alpha}} \left[\frac{6}{\alpha} \exp \left[\alpha \left(1 - \frac{r}{r_m} \right) \right] - \left(\frac{r_m}{r} \right)^6 \right] \quad r > r_{\max}$$

$$V = \infty \quad r < r_{\max}$$

where $r_{\max}$ is the value of r for which V has a spurious maximum. For the rare gases, α is of order 12-15, r_m and r_0 from 3-4 Å, and ϵ from .0026 to .0086 ev.

Data on various equilibrium properties of gases which involve the intermolecular potential have been used for potential fitting. These are: the transport coefficients of gases; the second virial coefficient, which appears in the equation of state; and crystal data - the equation for the heat of sublimation at 0 °K, and the equation for the crystal lattice spacing.

There are two objections to the use of these data in attempting to fit (7) or (8) to any molecular system: first, these data refer to equilibrium properties of gases and can only give information about the potential for relatively large values of separation of the molecules. In the study of inelastic collisions, however, we are interested in the potential for very small values of nuclear separation. Second, these equilibrium properties are not calculated directly from the

intermolecular potential, but rather indirectly by averaging over a large aggregate of molecules in interaction. This averaging procedure will introduce errors of its own, and as a result the constants in the potential will not be uniquely determined.

The transport coefficients of a gas are given as functions of the elastic cross section in the Chapman-Enskog theory of non-ideal gases. The relations between the transport properties and the cross sections are derived with the following assumptions: (1) only elastic binary collisions occur; (2) classical mechanics is valid; the effects of quantum mechanics are assumed to be insignificant. In addition, a spherically symmetric potential is postulated in order to carry out the integrations. The assumption of binary collisions limits the method to gases of moderately low density. The neglect of inelastic scattering makes it impossible to calculate, for example, the coefficient of thermal conductivity for a gas that can transport energy via its internal degrees of freedom, e.g., H_2 .* The use of classical mechanics restricts the theory to gas temperatures high enough that quantum effects are indeed negligible. These limitations are not unduly restrictive for most molecules of interest. Only in the case of He or H_2 at low temperature does the theory fail.

The equation of state of a non-ideal gas at moderately low density is given by the equation

$$(9) \quad pV = nkT(1 + \frac{B}{V} + \frac{C}{V^2} + \dots)$$

where B and C are functions of the temperature T and of the intermolecular potential. If classical mechanics is used in deriving (9), then B and C are given by

$$(10) \quad \begin{aligned} B &= \frac{1}{2} \int f(r_{12}) d\tau \\ C &= \frac{1}{3} \int \int f(r_{12}) \cdot f(r_{13}) \cdot f(r_{23}) d\tau_1 d\tau_2 \end{aligned}$$

where $f(r) = 1 - e^{-U(r)/kT}$ and $U(r)$ is the interatomic potential.

* H_2 is anomalous, anyway.

For a spherically symmetric potential,

$$(11) \quad B = 2\pi \int_0^{\infty} r^2 (1 - e^{-U(r)/kT}) dr .$$

Since B/V is much greater than C/V^2 at normal pressures, and the equation for B is much simpler than that for C , most use has been made of data for B , the second virial coefficient.

Various difficulties arose in the attempt to make a reasonable fit of the Lennard-Jones potential (7) to some simple molecular systems. T. Kihara^[14] evaluated the third virial coefficient for the rare gases using the Lennard-Jones potential and found that the potential bowl was too narrow. This is to be expected, since the repulsive r^{-12} term is not accurate over a large range of distances. The correct potential behaves near the origin like r^{-1} rather than like r^{-12} . It has been found impossible to fit the data on viscosity^[15] for H_2 , CO_2 , and He over the complete range of temperatures for which data is available. The parameter ϵ in (7) must vary with temperature if the data is to be fit for moderate and high temperatures simultaneously. Yntema and Schneider^[16] encountered similar problems in fitting the second virial coefficient data of He. Amdur, Ross and Mason^[17] found that two different sets of values of (r_0, ϵ) were necessary in order to fit the second virial data of CO_2 over the entire range $0 < T < 600^\circ C$.

These difficulties have led to the investigation of the more realistic exponential-six potential (8). The exponential form is known to be a better approximation to the repulsive part of the intermolecular potential than the form λr^{-n} .

Mason and Rice have fitted exponential-six and Lennard-Jones 12-6 potentials to He and H_2 data.^[18] Here, the quantum corrections to the second virial coefficient and coefficient of viscosity are significant, but unfortunately can only be estimated. The results seem to indicate a better agreement with the experimental data on He for the exponential-six than for the Lennard-Jones potential. The exponential-six result fits the data on viscosity very well at high temperature,

whereas the Lennard-Jones potential gives too small a result for temperatures greater than about 800°K. This result with the Lennard-Jones potential was also obtained by Whalley and Schneider. [15] The thermal conductivity does not fit particularly well with the exponential-six potential although it is better than the Lennard-Jones. Similar results are obtained for H₂, except that the thermal conductivity can not be fitted with the classical theory used here. Some typical results for the He and H₂ are shown in Table I.

	He		H ₂	
	Exp-six	L.-J.(12-6)	Exp-six	L.-J.(12-6)
α	12.4	...	14.0	...
r_m, a_0	5.93	5.43	6.32	6.22
$\epsilon/k, ^\circ K$	9.16	10.22	37.3	37.0

Table I

For the rare gases Ne, Ar, Kr, and Xe, Mason and Rice [19] used crystal data to find r_m and ϵ as a function of α , and then fitted α to data on viscosity and second virial coefficient. The results are in good agreement with experiment. However, for these rare gases a Lennard-Jones potential gave almost the same results. It was not found possible to obtain a good fit to the data on viscosity with either of the two potentials. This result was also obtained by Whalley and Schneider. [20]

In an attempt to resolve the difficulties in fitting viscosity data, Whalley and Schneider reconsider the problem of fitting the exponential-six and Lennard-Jones potentials to Kr, Ar, and Xe. They reject the use of crystal data for the following reason. The theoretical formulas for the dependence of the crystal lattice spacing and heat of sublimation on the intermolecular potential are both derived on the assumption of the additivity of the potential. This means that the total potential energy of an assemblage of molecules is taken as the sum

of the potential energies between isolated pairs of molecules. This assumption was investigated by T. Kihara^[14] and Jansen and Dawson^[21] who found it led to incorrect conclusions about crystal structure. Whalley and Schneider reject the use of crystal data and use only second virial coefficient data in order to evaluate the parameters in exponential-six, 12-6, and 9-6 potentials.

A significant fact emerges from the calculations of Whalley and Schneider. All the potentials used fit the virial data well. On the other hand, for the three potentials investigated, there is a large spread in the values of ϵ/k , and a spread of nearly 10% in the values of r_m . For argon, ϵ/k ranges from 89.6 °K for a 9-6 potential to 131.5 °K for an exponential-six potential. r_m varies from 4.08 to 3.78 Å. Similar results are obtained for Kr and Xe.

Whalley and Schneider conclude that the coefficient of viscosity is relatively insensitive to the exact details of the interaction and can be moderately well predicted by a single choice of ϵ and r_0 . The reason is that the main part of the temperature variation of the coefficient of viscosity is proportional to the square root of the temperature, whereas the part depending on the details of the intermolecular potential is a relatively slowly varying function over a large range of temperature.

It thus appears that it is not possible to obtain a unique determination of the parameters for an intermolecular potential by fitting to transport and second virial coefficient data. The averaging procedure that is necessary in order to go from the properties of an isolated molecular pair to the properties of a gas also smooths out the details of the interaction of the isolated molecular pair.

1.32 Scattering experiments

It is also possible to fit an intermolecular potential by use of scattering data. This would seem to be a more satisfactory procedure than fitting to macroscopic data such as transport coefficients. Scattering cross sections reflect the interaction of individual molecular systems directly, and no averaging over a large assemblage of interacting systems need be made. This reduces the chances for error as well as increases the possibility of obtaining a better determination of the parameters.

Unfortunately, little molecular scattering data is available. This is due to the difficulty in carrying out molecular scattering experiments at the low energies of interest. Some scattering data have been collected for alkali atom-rare gas collisions because of the convenience and accuracy of the hot wire method of detection that can be used. The results are useful in estimating the van der Waal's constant, if an asymptotic potential of the form $-C/r^6$ is used to fit the scattering data.

Recently Amdur and Mason, in a series of papers, have reported the cross section for scattering of the rare gases A-A^[22], Ne-Ne^[23], Kr-Kr^[24], and He-He^{[25], [26]} in the energy range from 500 to 2000 ev. They have been able to fit a potential of the form $V(r) = K/r^s$ to the data obtained, using classical scattering theory. The potentials so obtained, which fit the data very well, are valid in the region $0.5 \text{ \AA} < r < 2 \text{ \AA}$, approximately. Representative values of K and s are shown in Table II.

	K	s	Range of validity
A	$1.36 \cdot 10^{-9}$	8.33	$2.18 \text{ \AA} < r < 2.98 \text{ \AA}$
N	$5.10 \cdot 10^{-10}$	9.99	$1.76 \text{ \AA} < r < 2.32 \text{ \AA}$
Kr	$2.55 \cdot 10^{-10}$	5.42	$2.42 \text{ \AA} < r < 3.14 \text{ \AA}$
He	$7.55 \cdot 10^{-12}$	5.94	$1.27 \text{ \AA} < r < 1.59 \text{ \AA}$

Table II. Constants K and s for the intermolecular potential $V = K/r^s$ derived from scattering data. (V in ergs, r in angstroms.)

1.33 The potential between two hydrogen molecules

The interaction of two hydrogen molecules has been calculated analytically by means of a variational method. Because of the way the calculation is performed, the interaction can be written as the sum of four terms: the valence energy due to the overlap of the wave functions; the electrostatic quadrupole-quadrupole interaction energy; and the two dispersion energy terms varying as the inverse sixth and eighth powers of the nuclear separation.

The valence energy is the most difficult part to calculate. Very many exchange integrals must be calculated whether a perturbation or variational treatment is used. DeBoer^[27] used a first order perturbation (Heitler-London) method, but neglected all exchange integrals. Evett and Margenau^[13] did a similar calculation but included estimates on the exchange integrals. The result for the valence energy is a complicated function of the orientation of the two molecules.

The long range energy of interaction is much easier to calculate. An accurate calculation of the quadrupole-quadrupole interaction was made by James and Coolidge^[28] using a thirteen term wave function. Margenau^[13] obtained a good calculation of the inverse sixth power dispersion energy averaged over all orientations of the two molecules. The contribution of the inverse eighth power dispersion energy to the total interaction is very small, and has been calculated as a function of nuclear separation only.

The result of all these calculations gives an energy of interaction averaged over all molecular orientations which is in good agreement with the experimental energy calculated from compressibility data^[29]. The potential has a zero at $5.7 a_0$ and a minimum at $6.4 a_0$. Much effort has been directed at obtaining reliable values of the energy for molecular separation from 5 to $10 a_0$. This is the region of interest for low energy collisions which are important in

calculating macroscopic properties of gases (transport coefficients, and the second virial coefficient). However, for inelastic collisions it is necessary to know the potential in the region 2.5 to $5 a_0$.

We use the potential of Evett and Margenau in the way E. Bauer did. A Morse or exponential-six form can be fitted to the calculated potential by matching the zero and minimum of the potential, and the slope at $V = 0$. In this way we obtain a reasonable approximation to the potential in the important region from 2 to $5 a_0$.

2. Inelastic scattering for H_2-H_2

2.1 Formulation

2.1.1 The perturbation scheme and the potentials [6]

Consider a molecule AB colliding with another molecule (or atom) C. So far as the nuclear motion is concerned, A, B, and C are regarded as point particles moving in a potential field which is determined by the orbital electrons. This is the adiabatic approximation discussed in Section 1, p. 1.

We use the coordinates of (1). For a collision between two hydrogen molecules, $A = B = M_H$, and $C = 2A = 2M_H$. Hence the reduced masses of (2) become

$$(12) \quad M_1 = M_H/2 ; \quad M_e = M_H .$$

We shall consider only collinear collisions in the present work. The introduction of non-collinear collisions would greatly complicate the calculation by bringing in more independent variables. Since we do not know the intermolecular potential very well, we shall use a simple model, i.e., a spherically symmetric potential. The potential is given by (3):

$$(13) \quad v(\vec{r}, \vec{p}) = v_1^0(\vec{r}_0, \vec{p}) + v_e^0(\vec{r}, \vec{p}_0) + v'(\vec{r}; \vec{p}_0; \vec{p} - \vec{p}_0) .$$

We assume that V' is very much smaller than V_e^0 . Its specific form will be discussed below.

Since we are concerned with a transition from the ground to the first excited vibrational state, the assumption of a harmonic oscillator potential for $V_i^0(\vec{r}_0, \vec{\rho})$ will be good. Thus we take

$$(14) \quad V_i^0(\vec{r}_0, \rho) = \frac{M_i}{2} \omega^2 (\vec{\rho} - \vec{\rho}_0)^2.$$

This form for the potential V_i^0 leads to a simplification of the perturbation potential V' .

We use the same scheme for the perturbation potential that has been described by Zener [7], [9] and Bauer [6]. The perturbation potential arises from the expansion of $V_e^0(\vec{r}, \vec{\rho})$ in a Taylor's series about $\rho = \rho_0$:

$$(15) \quad V_e^0(\vec{r}, \vec{\rho}) = V_e^0(\vec{r}, \vec{\rho}_0) + (\rho - \rho_0) \left(\frac{dV_e^0}{d\rho} \right)_{\rho=\rho_0} + \frac{1}{2} (\rho - \rho_0)^2 \left(\frac{d^2 V_e^0}{d\rho^2} \right)_{\rho=\rho_0} + \dots$$

The first term on the right is the unperturbed potential which appears in (13). All the terms beyond the first constitute the perturbation potential. However, for harmonic oscillator wave functions, the matrix element of $(\rho - \rho_0)^n$ between the m -th and $(m+1)$ -st state vanishes unless $n = 1$. Hence all the terms in (15) of higher order than $(\rho - \rho_0)$ give no contribution to the inelastic scattering cross section. The effective perturbation potential is then

$$(16) \quad V'(\vec{r}; \vec{\rho}_0; \rho - \rho_0) = (\rho - \rho_0) \left(\frac{dV_e^0}{d\rho} \right)_{\rho=\rho_0}.$$

Thus the effect of the harmonic oscillator approximation to V_i^0 is to make the perturbation potential a separable function of $\vec{\rho}$ and $\vec{r}$. This will considerably simplify the perturbation scheme to be adopted.

We are concerned with a transition from the ground to the first excited

vibrational state. No rotational states are excited, so that conservation of energy takes the form

$$(17) \quad \hbar(\omega_f - \omega_o) = (k_o^2 - k_f^2) \hbar^2 / 2M_e .$$

For the first vibrational state of H_2 :

$$(18) \quad \hbar(\omega_f - \omega_o) = 20.10^{-3} e^2/a_o = 0.54 \text{ ev} .$$

A Morse potential of the form

$$(19) \quad V_M = U_o \left[e^{-2a(r-x)} - e^{-a(r-x)} \right]$$

is substituted into $V_e^o(\vec{r}, \vec{\rho})$ which is taken as

$$(20) \quad V_e^o(\vec{r}, \vec{\rho}) = V_m(\vec{r}_{AC}) + V_M(\vec{r}_{BC})$$

where

$$(21) \quad \vec{r}_{AC} = \vec{r} - \vec{\rho}/2 ; \quad \vec{r}_{BC} = \vec{r} + \vec{\rho}/2 .$$

This gives

$$(22) \quad V_e^o(\vec{r}, \vec{\rho}) = 2U_o \left[\cosh a\rho e^{-2a(r-x)} - \cosh \frac{a\rho}{2} e^{-a(r-x)} \right] .$$

We write this in the alternate form

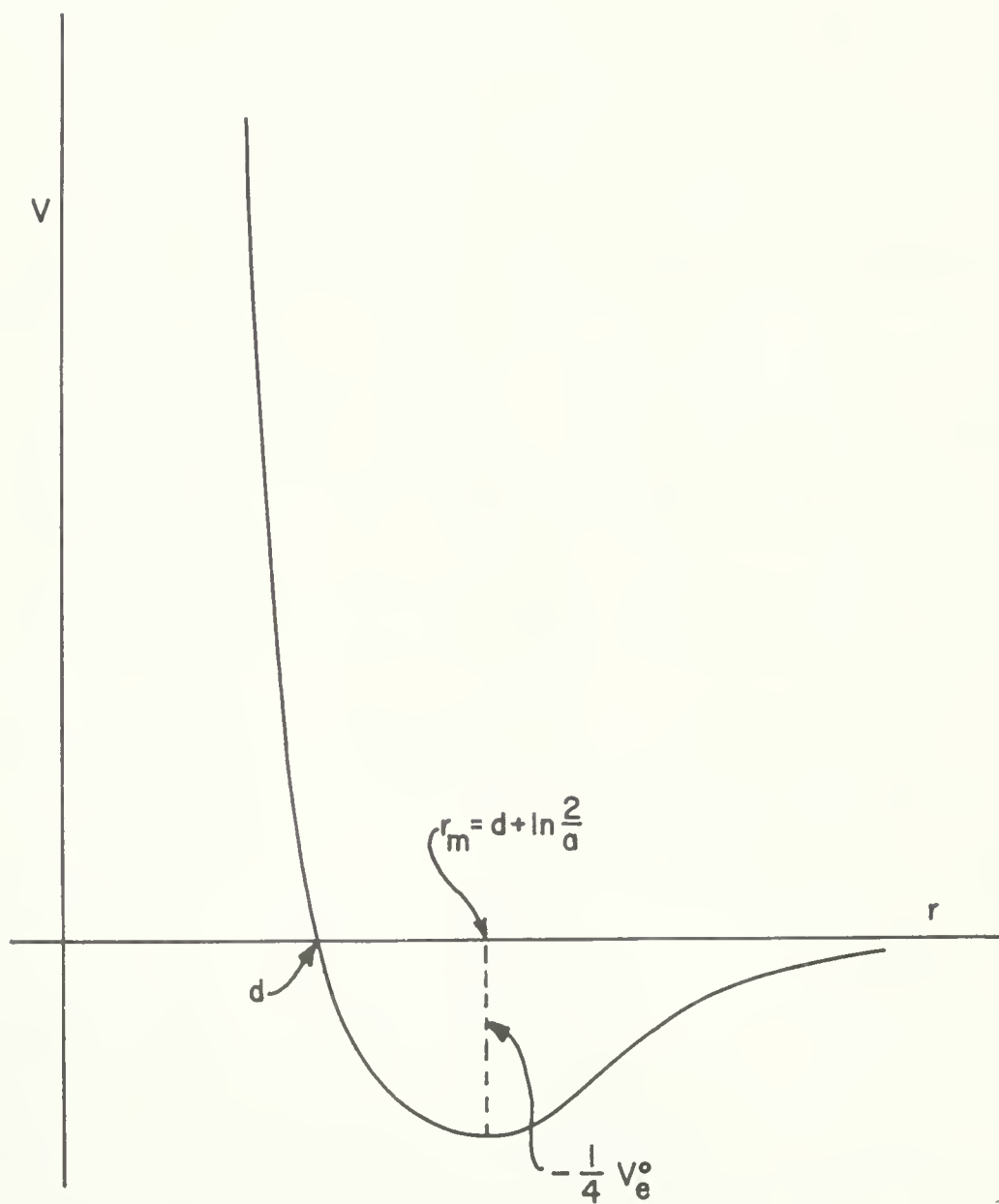
$$(23) \quad V_e^o(\vec{r}, \vec{\rho}_o) = U_e^o \left[e^{-2a(r-d)} - e^{-a(r-d)} \right]$$

$$U_e^o = 2U_o \left[\cosh a\rho_o/2 \right]^2 / \cosh a\rho_o ; \quad d = x + \frac{1}{a} \ln \frac{\cosh a\rho_o}{\cosh a\rho_o/2} .$$

The constants are chosen to fit the best data of Evett and Margenau^[13]:

$$(24) \quad U_e^o = 4.18 \cdot 10^{-4} \frac{e^2}{a_o} ; \quad a = .916 a_o^{-1} ; \quad d = 5.67 a_o .$$

$V_e^o(r, \rho_o)$ has the general shape shown in Figure 2, with a zero at $r = d = 5.67 a_o$, and a minimum of $-\frac{1}{4} U_e^o = -.003 \text{ ev}$ at $r = d + \ln 2/a = 6.42 a_o$.



Intermolecular Potential $V_e^o(r, \rho_o)$

Figure 2

From (16) the perturbation potential is

$$(25) \quad V'(\vec{r}; \vec{\rho}_0; \vec{p}-\vec{p}_0) = (\rho-\rho_0)U_0 a \left[2 \sinh a\rho e^{-2a(r-x)} - \sinh \frac{a\rho}{2} e^{-a(r-x)} \right]$$

which can be written as

$$(26) \quad V'(\vec{r}; \vec{\rho}_0; \vec{p}-\vec{p}_0) = (\rho-\rho_0)U' a \left[e^{-2a(r-z)} - e^{-a(r-z)} \right]$$

where

$$U' a (\rho-\rho_0)_{01} = 5.86 \cdot 10^{-6} e^2/a_0; \quad z = 6.87 a_0 .$$

Here $(\rho-\rho_0)_{01}$ is the matrix element of $(\rho-\rho_0)$ between the ground and first excited vibrational states.

2.12 The wave equation

With the coordinates (1) described above, the motion of the center of mass separates out and the total Hamiltonian becomes

$$(27) \quad H(\vec{r}, \vec{p}) = -\frac{\hbar^2}{2M_i} \nabla_\rho^2 - \frac{\hbar^2}{2M_e} \nabla_r^2 + V_i^0(\vec{r}_0, \rho) + V_e^0(\vec{r}, \rho_0) + V'(\vec{r}; \vec{\rho}_0; \vec{p}-\vec{p}_0) .$$

Since the perturbation potential V' is separable in ρ and r as we see from (26), we can separate the Schrödinger equation by writing the eigenstates of the unperturbed system as:

$$(28) \quad \Psi = \sum_j \phi_j(\vec{\rho}) \Psi_j(\vec{r})$$

where ϕ_j and Ψ_j are solutions of

$$(29) \quad \left(-\frac{\hbar^2}{2M_i} \nabla_\rho^2 + V_i^0(\vec{r}_0, \rho) - E_j \right) \phi_j(\vec{\rho}) = 0; \quad E_j = \hbar \omega_j$$

$$(30) \quad \left(-\frac{\hbar^2}{2M_e} \nabla_r^2 + V_e^0(\vec{r}, \rho_0) - \frac{\hbar^2 k^2}{2M_e} \right) \Psi_j(\vec{r}) = 0 .$$

We treat the ϕ 's as known harmonic oscillator wave functions, and the potential V' as a perturbation. Our problem is to solve (30) for the $\Psi_j(\vec{r})$ and calculate the inelastic cross section with these solutions.

Let us expand the functions $\Psi_j(\vec{r})$ in a series of spherical harmonics:

$$(31) \quad \Psi_j(\vec{r}) = \sum_{\ell} (2\ell + 1) P_{\ell}(\cos \theta_j) \chi_{\ell}(r)/r \quad j = 0, f.$$

Substituting into (30) we have

$$(32) \quad \frac{d^2 \chi_{\ell}}{dr^2} + \left[k_j^2 - \frac{2M_e}{\hbar^2} \left\{ V_e^0(\vec{r}, \rho_0) \right\} - \frac{\ell(\ell+1)}{r^2} \right] \chi_{\ell} = 0.$$

We use perturbation theory in order to obtain the inelastic cross section.

Given the Hamiltonian

$$H = H_0 + H' \quad \text{where } H' \ll H_0$$

and

$$(H_0 - E_n) u_n(r) = 0,$$

first order perturbation theory gives for the transition probability p_{f0} that the system will be found in a state f with eigenfunction u_f

$$p_{f0} = \frac{2\pi}{\hbar} |H'_{f0}|^2 \rho_f$$

where $\rho_f dE_f$ is the number of states in a range dE_f about E_f , and

$$H'_{f0} = \int \bar{u}_f(r) H'(r) u_0(r) d\tau.$$

Following Schiff^[30] we obtain for the cross section

$$(33) \quad d\sigma(\alpha, \beta) = \left(\frac{\mu}{2\pi\hbar^2} \right)^2 \frac{k_f}{k_0} |H'_{f0}|^2 d(\cos \alpha) d\beta.$$

In order to determine the normalization of the functions $\chi_{\ell}(r)$, we shall calculate the cross section from (33) in the Born approximation, in which case the solution $\Psi_j(\vec{r})$ of (30) is just a plane wave for both the initial and final states. We write these plane waves in a series of spherical harmonics, using the well known expansion

$$(34) \quad e^{ik_o r} = \sum_{\ell} (2\ell + 1) i^{\ell} P_{\ell}(\cos \theta_o) j_{\ell}(k_o r)$$

$$(35) \quad e^{ik_f r} = \sum_{\ell} (2\ell + 1) i^{\ell} P_{\ell}(\cos \theta_f) j_{\ell}(k_f r) \quad .$$

Here we take the z-axis along k_o . θ_o is the angle between k_o and r , and θ_f the angle between k_f and r . Then

$$(36) \quad H'_{fo} = \int \sum_{\ell} \sum_{\ell'} (2\ell + 1)(2\ell' + 1) i^{\ell - \ell'} P_{\ell}(\cos \theta_o) P_{\ell'}(\cos \theta_f) d(\cos \theta_o) d\phi_o V'_{fo}$$

where

$$(37) \quad V'_{fo} = \int_0^{\infty} j_{\ell}(k_o r) V'(r) j_{\ell}(k_f r) r^2 dr \quad .$$

From the addition theorem for spherical harmonics,

$$(38) \quad P_{\ell'}(\cos \theta_f) = \sum_m \frac{(\ell' - m)!}{(\ell' + m)!} P_{\ell'}^m(\cos \theta_o) P_{\ell'}^m(\cos \alpha) \cos m\beta$$

where

$$\cos \alpha = \cos \theta_o \cos \theta_f + \sin \theta_o \sin \theta_f \cos \beta$$

i.e., (α, β) is the angle between k_o and k_f .

In the integration over ϕ_o in (36) only $m = 0$ from (38) will contribute. But then the integral over θ_o has the term $\left\{ P_{\ell}(\cos \theta_o) P_{\ell'}(\cos \theta_o) \right\} P_{\ell'}(\cos \alpha)$. This integral also vanishes unless $\ell = \ell'$; then (36) becomes

$$(39) \quad H'_{fo} = \int \sum_{\ell} (2\ell + 1)^2 P_{\ell}^2(\cos \theta_o) P_{\ell}(\cos \alpha) d(\cos \theta_o) d\phi_o V'_{fo}$$

$$(39) \quad H'_{fo} = \sum_{\ell} 4\pi (2\ell + 1) P_{\ell}(\cos \alpha) V'_{fo} \quad .$$

From (36)

$$d\sigma(\alpha, \beta) = \frac{k_f}{k_o} \left(\frac{\mu}{2\pi\hbar^2} \right)^2 \sum_{\ell} \sum_{\ell'} 16\pi^2 (2\ell + 1)(2\ell' + 1) P_{\ell}(\cos \alpha) P_{\ell'}(\cos \alpha) |V'_{fo}|^2$$

or

$$(40) \quad \sigma_{fo} = \frac{k_f}{k_i} \left(\frac{2\mu}{\hbar^2} \right)^2 4\pi \sum_{\ell} (2\ell + 1) |V'_{fo}|^2$$

since only $\ell = \ell'$ contributes because of the orthogonality of the P's.

The normalization here is determined by the asymptotic form of the spherical Bessel functions, j_ℓ , namely

$$(41) \quad j_\ell(kr) \xrightarrow{r \rightarrow \infty} \sin[kr - \ell\pi/2]/kr$$

and hence the plane waves of (34) and (35) have the asymptotic form

$$(42) \quad e^{ikr} \rightarrow \sum_{\ell} (2\ell+1)i^\ell P_\ell(\cos \theta) \sin[kr - \ell\pi/2]/kr.$$

The Born approximation is exact only if $V_e^0 = 0$, and V' sufficiently small. With a non-zero potential $V_e^0(r, \rho_0)$ present, (31) is the correct solution of the Schrödinger equation. Then the cross section derived above in the Born approximation holds also for the case $V_e^0 \neq 0$, with

$$(43) \quad v'_{fo} = \int_0^\infty \chi_\ell(k_o r) V'(r) \chi_\ell(k_f r) dr$$

instead of (37). Now the potential for the H_2-H_2 system goes to zero for large r . Hence asymptotically (31) must approach (42). Thus the normalization of the χ_ℓ 's, which are the solutions of (32), is determined by

$$(44) \quad \chi_\ell(r) \xrightarrow{r \rightarrow \infty} \frac{1}{k_j} \sin[k_j r + \delta_{j\ell} - \ell\pi/2], \quad j = 0, f,$$

where the phase shift $\delta_{j\ell}$ represents the effect of the potential.

It will be noted that, (40), the cross section in the Born approximation, expressed as a sum over phases, reduces to the usual form of the Born approximation if we carry out the sums and integrations. The usual form of the cross section in the Born approximation is

$$(45) \quad d\sigma(\alpha) = \left(\frac{2\mu}{\hbar^2} \right)^2 \frac{k_f}{k_o} \left| \int_0^\infty \frac{\sin Kr}{Kr} V'(r) r^2 dr \right|^2 d(\cos \alpha)$$

where $K^2 = k_o^2 + k_f^2 - 2k_o k_f \cos \alpha$. From (37) we have for v'_{fo}

$$v'_{fo} = \int_0^\infty j_\ell(k_o r) V'(r) j_\ell(k_f r) r^2 dr.$$

Substituting this into (39)

$$(46) \quad H'_{fo} = 4\pi \int_0^{\infty} r^2 dr \sum_{\ell} (2\ell+1) j_{\ell}(k_o r) V'(r) j_{\ell}(k_f r) P_{\ell}(\cos \alpha) .$$

The sum can be written in closed form since [31]

$$\sum_{\ell} (2\ell+1) j_{\ell}(k_o r) j_{\ell}(k_f r) P_{\ell}(\cos \alpha) = \frac{\sin Kr}{Kr} .$$

Substituting this into (46), we have

$$H'_{fo} = 4\pi \int_0^{\infty} r^2 dr V'(r) \frac{\sin Kr}{Kr} .$$

Then the cross section (33) becomes

$$d\sigma(\alpha, \beta) = 4\pi \left(\frac{\mu}{2\pi\hbar^2} \right)^2 \frac{k_f}{k_o} \left| \int_0^{\infty} r^2 dr V'(r) \frac{\sin Kr}{Kr} \right|^2 d(\cos \alpha) d\beta .$$

Integrating out β ,

$$d\sigma(\alpha) = \left(\frac{2\mu}{\hbar^2} \right)^2 \frac{k_f}{k_o} \left| \int_0^{\infty} r^2 dr V'(r) \frac{\sin Kr}{Kr} \right|^2 d(\cos \alpha)$$

which is just (45).

Summary

We now have the following scheme: the cross section for inelastic scattering is given by

$$(47) \quad \sigma_{fo} = \frac{k_f}{k_o} \left(\frac{2\mu}{\hbar^2} \right)^2 \sum_{\ell} 4\pi (2\ell+1) |v'_{fo}|^2$$

where

$$(48) \quad v'_{fo} = \int_0^{\infty} \chi_{\ell}(k_o r) V'(r) \chi_{\ell}(k_f r) dr$$

and

$$(49) \quad \chi_{\ell}(r) \xrightarrow{r \rightarrow \infty} \frac{1}{k_j} \sin[k_j r + \delta_{j\ell} - \ell\pi/2] \quad j = 0, f .$$

The functions χ_{ℓ} are the solutions of the equation

$$(50) \quad \frac{d^2 \chi_{\ell}}{dr^2} + \left[k_j^2 - \frac{2M}{\hbar^2} V_{\theta}^o(r, \rho_o) - \frac{\ell(\ell+1)}{r^2} \right] \chi_{\ell} = 0 .$$

If we include the factors $1/k_j$ in the cross section rather than in the χ_ℓ , we have

$$(51) \quad \sigma_{fo} = \frac{l_1 \pi}{k_f k_o^3} \left(\frac{2\mu}{h^2} \right)^2 \sum_{\ell} (2\ell + 1) |v'_{fo}|^2 ,$$

$$(52) \quad \chi_\ell(k_j, r) \xrightarrow{r \rightarrow \infty} \sin \left[k_j r - \ell \pi/2 + \delta_{j\ell} \right] .$$

We convert to dimensionless units by substituting $x = kr$; then

$$(53) \quad \frac{d^2 \chi_\ell}{dx^2} + \left[1 - \frac{W^2}{S_j^2} M_e^0(x, \rho_o) - \frac{\ell(\ell+1)}{x^2} \right] \chi_\ell = 0 \quad j = 0, f$$

where

$$W^2 = 2M_e U_e^0 d^2 / h^2$$

$$S_j = k_j d$$

$$M_e^0(x, \rho_o) = e^{-2a'(x-S_j)} - e^{-a'(x-S_j)} \quad a' = a/k_j .$$

With these dimensionless units, (53) can be integrated on the Univac.

2.2 Integration of the radial equation on the Univac

We solved (53) by a modification of the Runge-Kutta integration scheme by S. Gill [32] which is particularly suitable for high speed digital computers. This scheme amounts to a Taylor's series expansion about a point $\underline{x}$, and in effect calculates the function and its derivative at a point $\underline{x} + h$ from the function and derivative at $\underline{x}$. The error of this scheme is of the order $h^5 f^{(v)}$ at any point, where h is the interval of integration and $f^{(v)}$ is the fifth derivative. Since $\max \chi_\ell^{(v)} = 1$, the error is h^5 at most. A sufficiently small interval h was used so that the error was less than $5 \cdot 10^{-4}$.

To obtain a starting value for the integration, we use the WKB solution of (53) as follows. Let x_0 be the solution of [33]

$$(54) \quad 1 - \frac{W^2}{S_j^2} M_e^0(x, \rho_0) - \frac{(\ell + 1/2)^2}{x^2} = 0.$$

For $\ell \gg 0$, x_0 is equivalent to the classical turning point of the motion in the potential given by (23). Then $x < x_0$, the WKB solution of (53) is

$$(55) \quad \chi_{\text{WKB}} \sim |Q^{-1/2}| \exp \left[- \int_x^{x_0} Q \, dx \right] \quad x < x_0$$

where

$$(56) \quad Q^2 = 1 - \frac{W^2}{S_j^2} M_e^0(x, \rho_0) - \frac{(\ell + 1/2)^2}{x^2}.$$

The solution in the region $x > x_0$ is given by

$$(57) \quad \chi_{\text{WKB}} \sim Q^{-1/2} \cos \left[\int_{x_0}^x Q \, dx - \frac{\pi}{4} \right] \quad x > x_0.$$

The WKB solution (55) was calculated beginning from $x = x_0$ and proceeding backwards towards $x = 0$ (i.e., $r = 0$). When the solution so obtained is less than 10^{-5} , we have reached the asymptotic region in which the WKB solution is valid. The starting values for the integration are χ_{wkb} and χ'_{wkb} at the first value of x , $x = x_i$, at which $\chi_{\text{wkb}} \leq 10^{-5}$. This assures us of not having neglected any significant contributions to V'_{f0} in (48) for $x < x_i$.

We now integrate (53) forward using the Runge-Kutta-Gill scheme. At the turning point, $x = x_0$, we compare the ratio of χ'/χ (where χ is the solution of (53)) with that predicted by the WKB-Langer approximation: [34]

$$(58) \quad \left(\frac{\chi'}{\chi} \right)_{\text{wkb}} = \frac{\Gamma(2/3) \sqrt[3]{3}}{\Gamma(1/3)} c^{1/3}, \quad c \equiv \left(\frac{dQ^2}{dx} \right)_{x=x_0}.$$

The two ratios disagree by about 2-3%, but this can probably be attributed to the inaccuracies of the approximation used to obtain (58), rather than to any inaccuracy in the Univac integration.

In the region $r \rightarrow \infty$, we know that the asymptotic form of the solution of (53) is given by (52). The asymptotic region is reached when the roots of χ_ℓ occur at a distance π apart. When this happens, the Univac program stops integrating the equation (53), which is relatively time-consuming, and produces the simple sine wave (51) with a proportionality constant determined by the preceding values of χ_ℓ at its peaks. The integration is ended at some fixed value of r ($12 a_0$) for which the value of V' in (26) is sufficiently small so that there will be no significant contribution to V'_{f0} in (48) from larger values of r .

As a check on the forward integration, the WKB solution, (57) was calculated simultaneously. After the asymptotic region of the WKB solution is reached, the values of x at the nodes and peaks of the WKB and R-K-G solutions differed by less than 10^{-3} . For a second check, the solution χ_ℓ was substituted back into the differential equation (53). A simple seven-point formula for the second derivative was used. The solution χ_ℓ was found to satisfy the differential equation to within an error of the order of 3 to $5 \cdot 10^{-4}$ at any point.

The calculation of the matrix elements V'_{f0} in (48) was carried out in a perfectly straightforward manner. The interval of integration h in the RKG integration scheme for the radial equation was so chosen that both $\chi_\ell(k_0 r)$ and $\chi_\ell(k_F r)$ in (48) were known for exactly the same values of r . This avoided any interpolation in the radial functions χ_ℓ . Hence V'_{f0} is calculated to exactly the same accuracy to which the χ_ℓ are known.

The total cross section is then found by integrating (51). A comparison with a summation rather than an integration over ℓ showed that the partial cross sections $\sigma_\ell = (2\ell + 1) |V'_{f0}|^2$ are a sufficiently smooth function of ℓ so that the integration was just as accurate as the summation.

2.3 Results

2.31 Results of Univac integration

The potentials used and typical radial functions are shown in Figure 3. The corrected result for the cross section obtained on the Univac is shown in Figure 4. The results obtained by E. Bauer are also shown. The correction to the Univac cross section comes about as follows.

The original results obtained using (51) are not flux-conserving at energies greater than about 5 ev. That is, the partial cross section of (51)

$$(59) \quad \sigma_{\ell} = \frac{4\pi}{k_f k_o^3} \left(\frac{2\mu}{\hbar^2} \right)^2 (2\ell+1) |v'_{fo}|^2$$

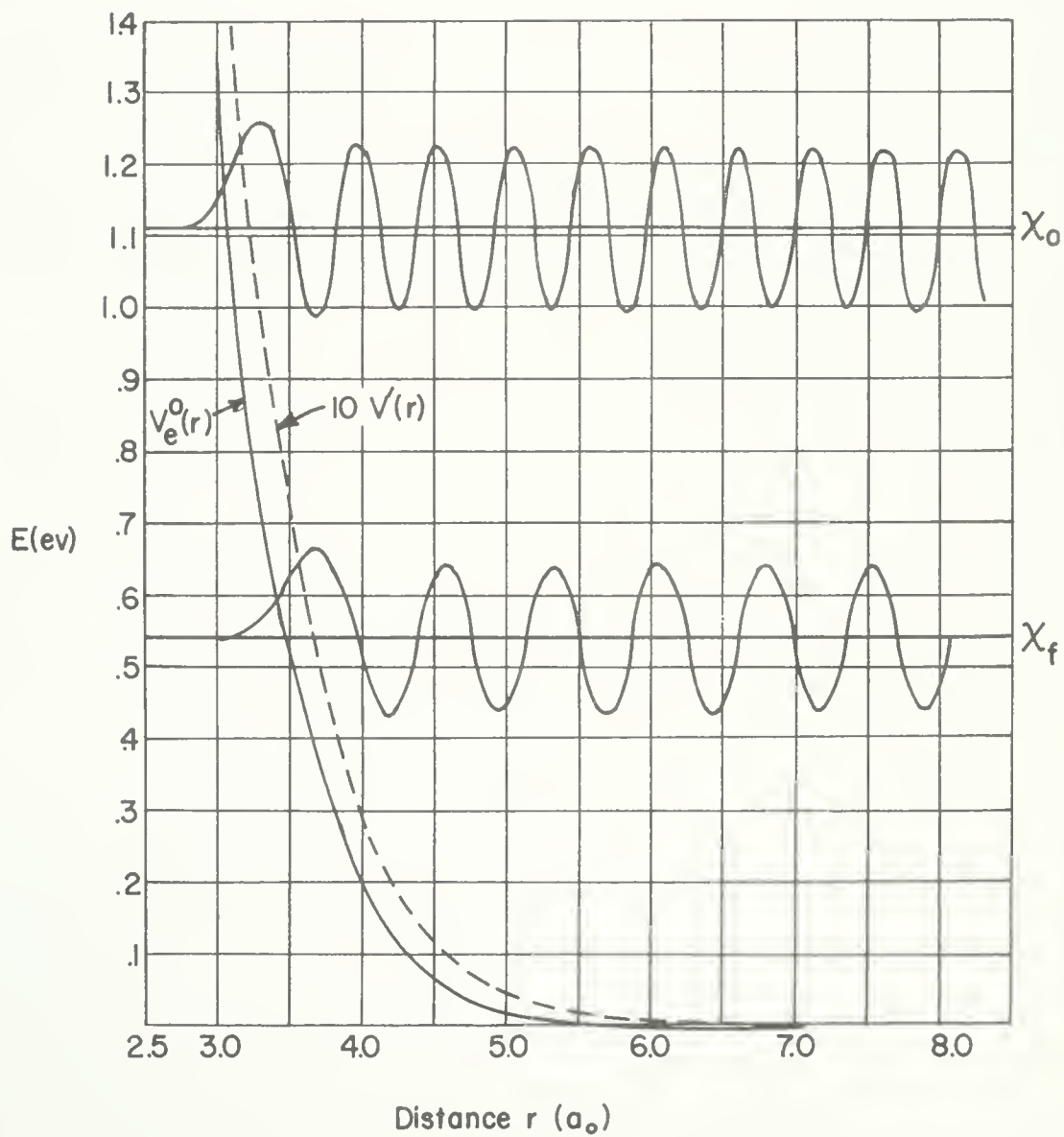
exceeds the maximum allowable value of the partial cross section [35],

$$(60) \quad \max \sigma_{\ell} = \frac{\pi}{k_o k_f} (2\ell+1) .$$

The partial cross section of (60) is the largest possible if the flux of particles is to be conserved.

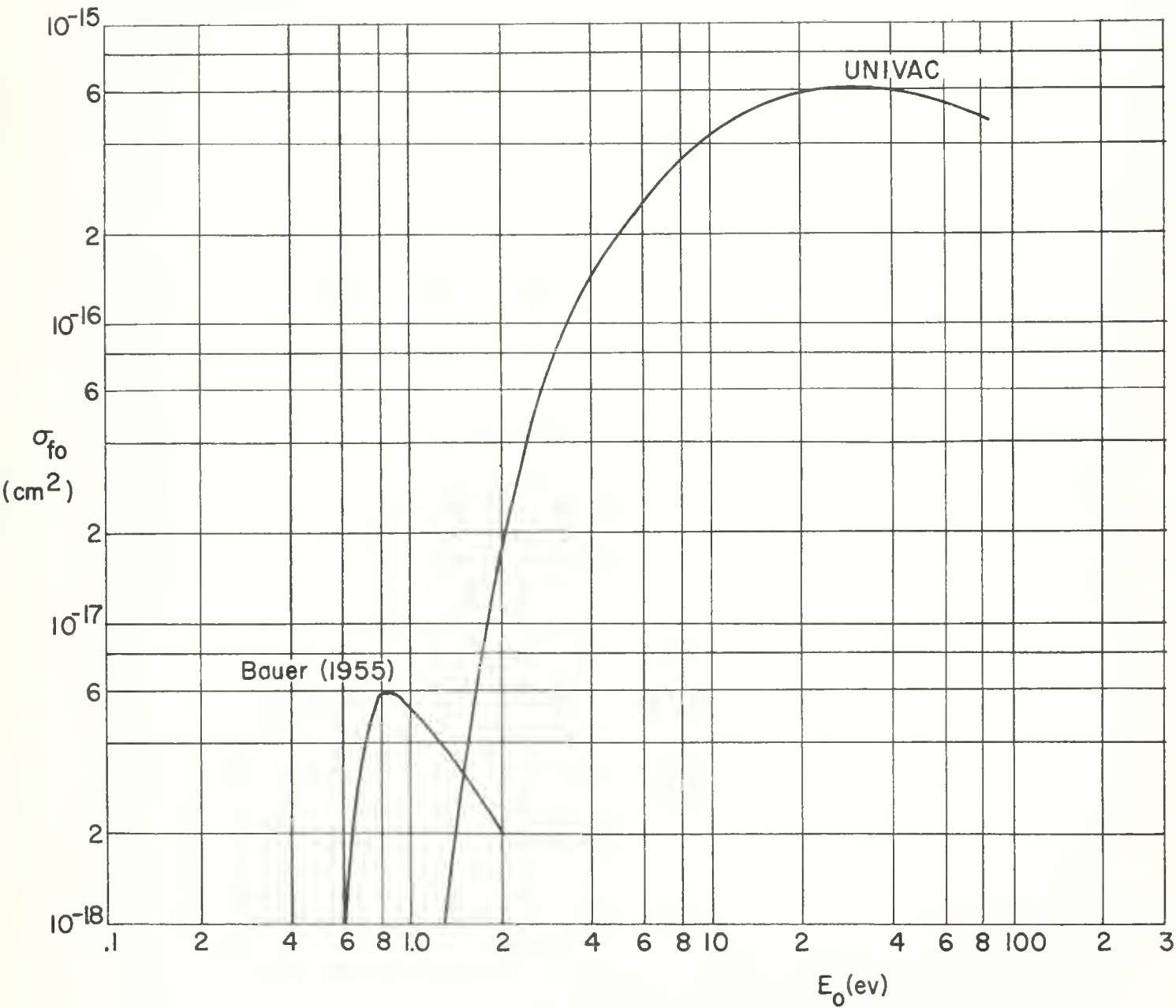
The violation of flux conservation at these high energies comes about because the molecules approach very closely at such energies. Then the wave functions will be appreciably large in the region where $v' \geq v_e^o$, i.e., near the origin. But the perturbation scheme used here is a reasonable approximation only as long as $v' \ll v_e^o$.

From a formal point of view, the violation of flux conservation arises because the scattering matrix of the perturbation scheme is not unitary. This can be corrected by working with the reaction matrix K instead of $T = S - 1$. The scattering matrix S is given by $1 - \frac{1}{2} iK/1 + \frac{1}{2} iK$, so that S is unitary so long as K is hermitian [36]. We have taken v'_{fo} to correspond to the eigenvalues of the reaction matrix K. Since these eigenvalues behave as $\tan \delta_{\ell}$, we replace $|v'_{fo}|^2$ by $|v'_{fo}|^2 / (1 + |v'_{fo}|^2)$, i.e., replace $\tan^2 \delta_{\ell}$ by $\sin^2 \delta_{\ell}$.



Potentials and initial and final wave functions
for $E_0 = 1.1 \text{ eV}$, $l = 0$

Figure 3



Total cross-section: UNIVAC and Bauer (1955) approximations
compared as functions of energy on log-log plot

Figure 4

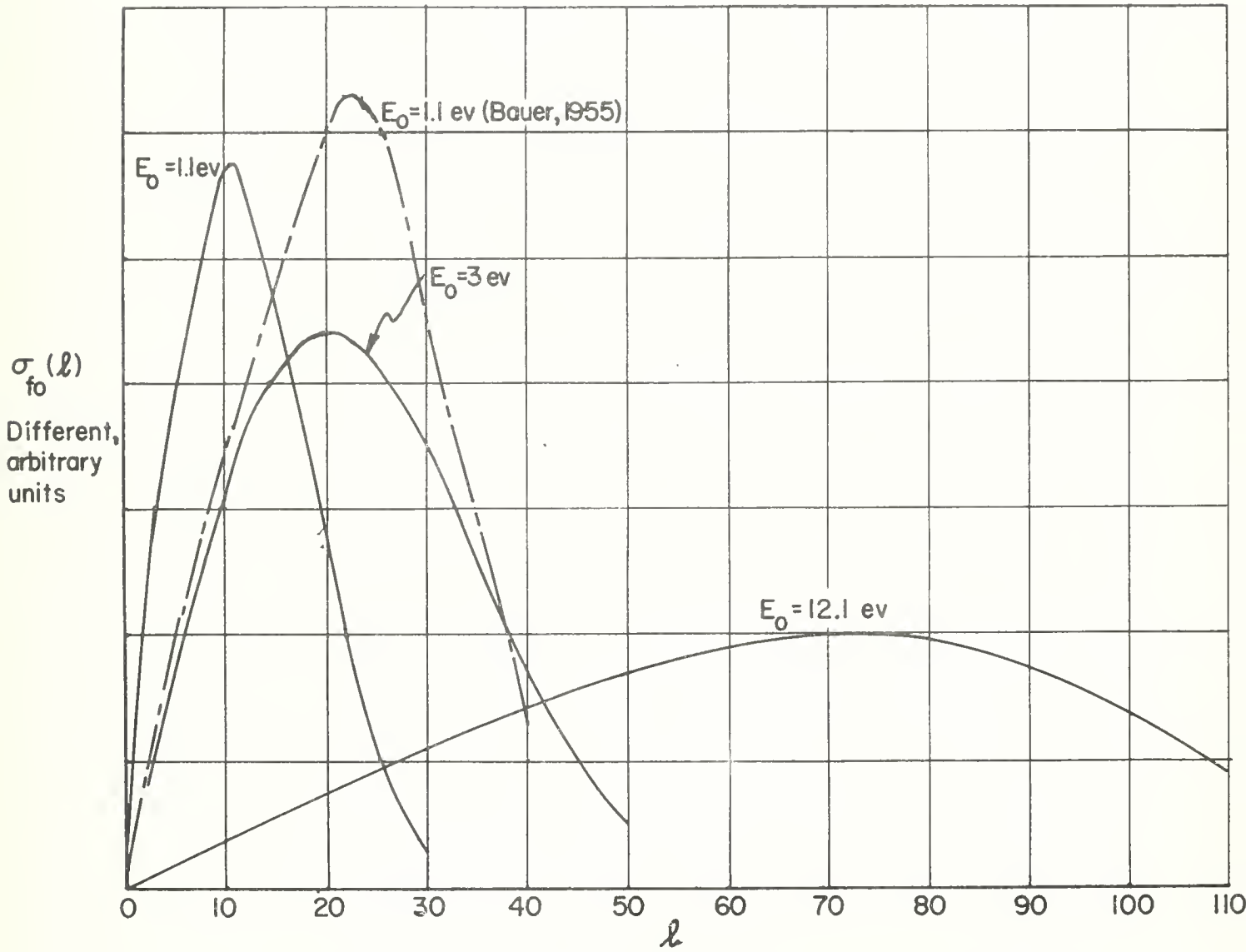
Then

$$(61) \quad \sigma_l = \frac{\pi}{k_o k_f} (2l+1) \frac{|v'_{fo}|^2}{1 + |v_{fo}|^2} \quad .$$

It is this corrected cross section which is shown in Figure 4. At the energies where this correction is needed, however, the inelastic cross section calculated in the present work is entirely incorrect. At these energies the probability of electronic transitions, which we have neglected, becomes significant. The inelastic cross section calculated here is consequently physically unrealistic for energies greater than 5 ev.

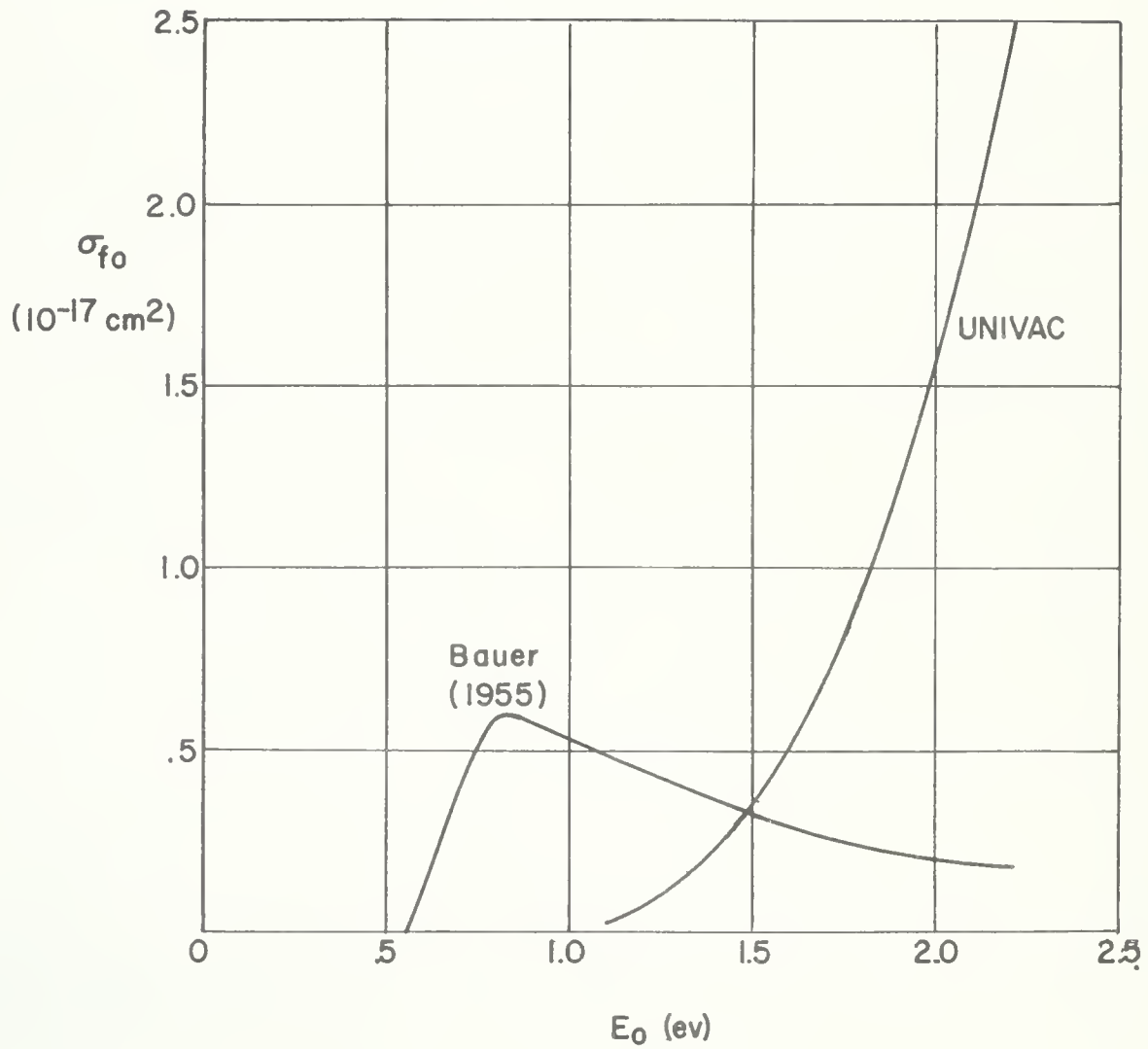
It is clear from Figure 4 that there is disagreement with the results of E. Bauer so far as the energy dependence of the cross section is concerned. The reasons for this have already been pointed out in Section 1, § 1.24. But we do verify here that one has to sum over many partial waves. This is shown in Figure 5 where the partial cross section is plotted as a function of l for both the present calculation and for the results of E. Bauer. In Figure 6 we have plotted on a linear scale the cross section obtained by the Univac and that of E. Bauer in the energy range near threshold, 0.5 to 2 ev.

To obtain checks on the energy dependence of the inelastic cross section, and in particular on the expected value of energy for which the cross section has a maximum, various approximate solutions to the problem have been considered. These are discussed in the following section. All these approximations indicate that the energy dependence of the inelastic cross section in Figure 4 is physically reasonable and that the maximum can be expected to occur at a relatively high energy.



Partial cross-section $\sigma_{fo}(l)$ as a function of angular momentum l
for various energies

Figure 5



Total cross-section: comparison of UNIVAC results with
Bauer (1955) for energies near the threshold

Figure 6.

2.32 Approximations

2.321 Resonance approximation

The intermolecular potential can be looked upon as a disturbing force applied to a simple harmonic oscillator of frequency ν , which is the molecule that can be excited to the first vibrational state. In order for any appreciable forced oscillation to be produced, the time collision, τ , should not be too great compared with the natural period $1/\nu$. Hence

$$(62) \quad \begin{array}{ll} \tau \nu \gg 1 & \text{weak excitation ,} \\ \tau \nu \sim 1 & \text{maximum excitation .} \end{array}$$

Since $\tau \sim d/v$ where d is the range of the intermolecular potential and v is the relative velocity of the colliding molecules, the condition for maximum excitation becomes

$$(63) \quad d v / v \sim 1 .$$

Writing $\nu = \Delta E/h$, we obtain $k \sim 30 \text{ \AA}^{-1}$ for a maximum cross section, or $E \sim 7 \text{ ev.}$ This energy is of the same order of magnitude as the actual maximum energy, 25 ev.

2.322 Born approximation

We calculate the cross section for inelastic scattering in the Born approximation using (45) for the cross section and (26) for the perturbation potential. The integrations can be carried out simply. The results are shown in Figure 7. It is seen that the maximum in the curve occurs at an initial energy of about 7 ev. As an independent check on this result, the cross section can be calculated from the alternate form of the Born approximation, (40), as a sum over phases. V'_{fo} is given by (37) and involves for the case of the Morse potential the integral

Born Approximation

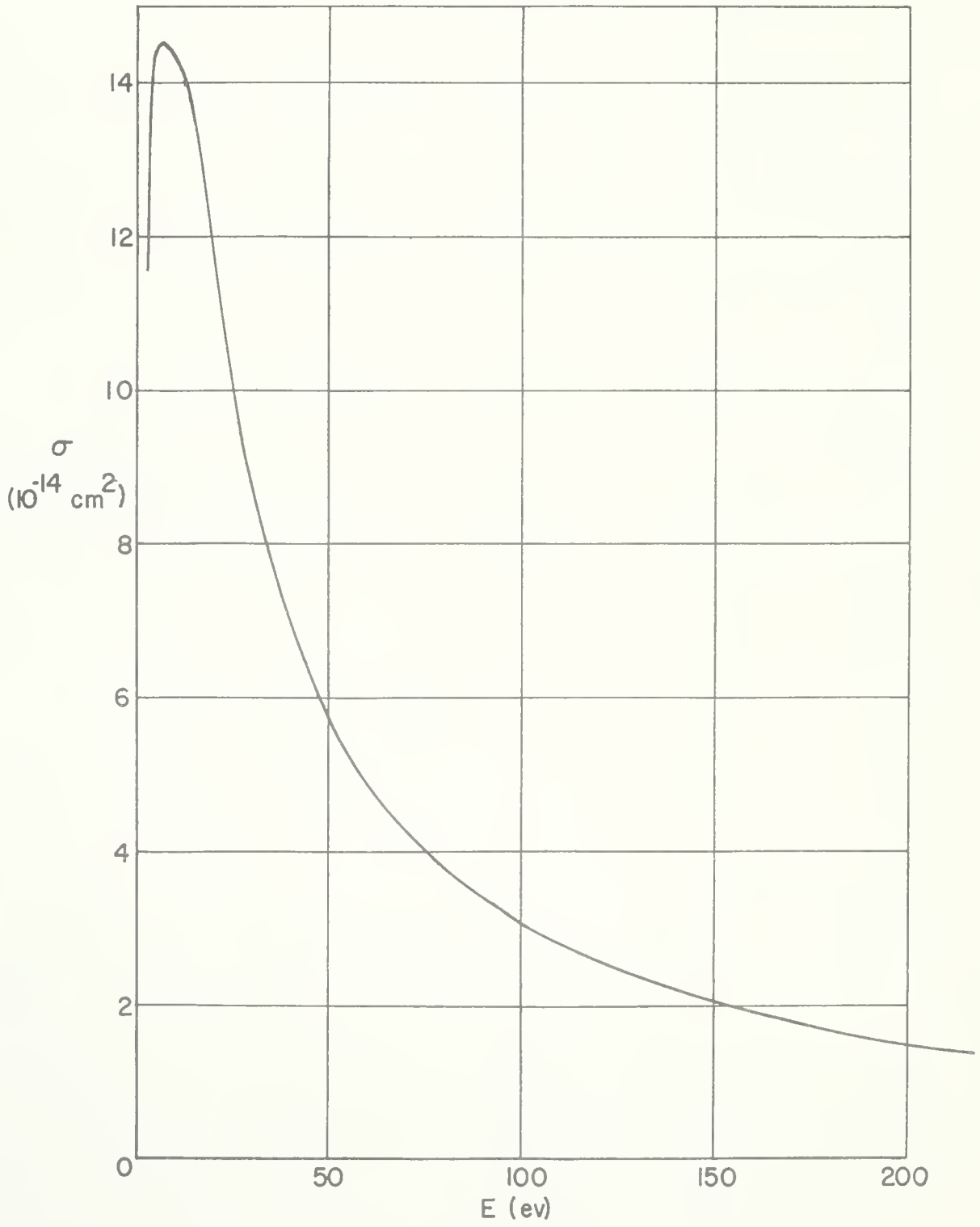


Figure 7

$$I = \int_0^{\infty} e^{-ar} j_{\ell}(k_o r) j_{\ell}(k_f r) r^2 dr$$

where

$$j_{\ell}(\rho) = (\pi/2\rho)^{1/2} J_{\ell+1/2}(\rho)$$

therefore

$$I = \frac{\pi}{2(k_o k_f)^{1/2}} \int_0^{\infty} e^{-ar} J_{\ell+1/2}(k_o r) J_{\ell+1/2}(k_f r) r dr.$$

This can be written in terms of Q_{ℓ} , the associated Legendre function of the second kind [37]

$$I = -\frac{a}{2(k_o k_f)^2} Q'_{\ell} \left(\frac{k_o^2 + k_f^2 + a^2}{2k_o k_f} \right)$$

where the prime denotes differentiation with respect to the argument. An expression for the cross section is obtained in terms of a sum over ℓ of these Legendre functions. This sum was evaluated for two energies, and the answers agreed with the simpler form of the Born approximation.

The Born approximation result in Figure 7 is not flux-conserving over the entire energy range of interest, that is, up to an energy so large that electronic transitions become significant. Furthermore, it is larger by several orders of magnitude at every value of energy than the cross section of Figure 4. Consequently, the Born approximation is of absolutely no use in calculating an inelastic cross section. However, as a mathematical approximation it does indicate the expected value of the energy for the maximum cross section.

2.323 High energy approximation

The radial equation we must solve is given by (53). It will be noted that if we approximate $V_e^o(r)$ by α/r^2 , where α is a positive constant, the solutions χ_{ℓ} become spherical Bessel functions of non-simple order. Furthermore, if we also approximate $V'(r)$ by β/r^2 then V'_{fo} in (48) can be written in closed form. In short, the cross section can be calculated analytically in this approximation.

This replacement of $V_0^0(r)$ by a/r^2 will surely not be good except at very high energies with initial energy greater than about 2 ev. However, this will give us an indication of the high energy behavior of the cross section.

Substituting $V_0^0(r) = a/r^2$ into (53)

$$(64) \quad \frac{d^2 \chi_\ell}{dx^2} + \left[1 - \frac{a' + \ell(\ell+1)}{x^2} \right] \chi_\ell = 0$$

where $a' = 2ma/\hbar^2$. (a must have dimensions energy-cm² in order for a/r^2 to have dimension energy, as it should. Hence a' is dimensionless.) The solution to (64) is

$$(65) \quad \chi_\ell = j_{\nu+1/2}(x)$$

which has the correct asymptotic form (49). Here

$$(66) \quad \begin{aligned} \nu(\nu+1) &= \ell(\ell+1) + a' \\ 2\nu + 1 &= 2[(\ell + 1/2)^2 + a']^{1/2} \end{aligned}$$

The positive root in (66) must be taken^[38] in order that χ_ℓ be finite at $r = 0$.

Substituting this solution into (48), we have

$$(67) \quad \begin{aligned} V'_{fo} &= \int_0^\infty \left(\frac{\pi}{2k_o r} \right)^{1/2} J_{\nu+1/2}(k_o r) \frac{\beta}{r^2} \left(\frac{\pi}{2k_f r} \right)^{1/2} J_{\nu+1/2}(k_f r) r^2 dr \\ &= \frac{\pi\beta}{2(k_o k_f)^{1/2}} \int_0^\infty \frac{dr}{r} J_{\nu+1/2}(k_o r) J_{\nu+1/2}(k_f r) \end{aligned}$$

This integral can be written in the closed form^[39]

$$\frac{1}{2} (k_f/k_o)^{\nu+1/2} / \nu+1/2$$

Hence

$$V'_{fo} = \frac{\pi\beta}{2(k_o k_f)^{1/2}} \frac{1}{2\nu+1} (k_f/k_o)^{\nu+1/2}$$

Then the cross section in (47) is just

$$(68) \quad \sigma = \left(\frac{\pi \mu \beta}{\hbar^2} \right)^2 \frac{4\pi}{k_0^2} \sum_{\ell} (2\ell+1) (k_f/k_0)^{2\nu+1} \frac{1}{(2\nu+1)^2} .$$

On comparing the values of the Morse potential of (23) with the approximation $1/r^2$, it is seen that a value of α' of about 5000 will give a fairly good correspondence between α/r^2 and $V_e^0(r)$. This value of α' will be good at least for energies high enough that the turning point is not greater than about $2.2a_0$. This will be true for energies greater than about 3 ev. The inelastic cross section was calculated from (68) with three different values of α' : 5000, 3000, and 7000. These are shown in Figure 8. It is clear that the large variation in the values of α' produces only a slight change in the position of the peak of the curve. The value of the cross section at the peak, however, varies greatly with the change in α' .

As a check on the accuracy of the cross section in this approximation, we can compare (68) with the cross section obtained from the Born approximation for a β/r^2 potential. In this case the cross section is given by (47). Since we are using $V' = \beta/r^2$, the integration for V'_{f0} is carried out like (67) with the only difference that we have ℓ now instead of ν :

$$(69) \quad \sigma = \left(\frac{\pi \mu \beta}{\hbar^2} \right)^2 \frac{4\pi}{k_0^2} \sum_{\ell} \frac{1}{2\ell+1} (k_f/k_0)^{2\ell+1} .$$

We see from (66) for $(2\nu+1)$ that if ℓ is large enough compared with α' that we can neglect α' , then

$$(2\nu+1) = 2 \left[(\ell+1/2)^2 + \alpha' \right]^{1/2} \xrightarrow{\ell \gg \alpha'} 2(\ell+1/2) = 2\ell+1 .$$

In this case (68) reduces to (69), as it should in the limit of high energies.

High Energy Computation

A: $\alpha' = 5000$

B: $\alpha' = 3000$

C: $\alpha' = 7000$

D: $\frac{1}{5}$ Born approximation

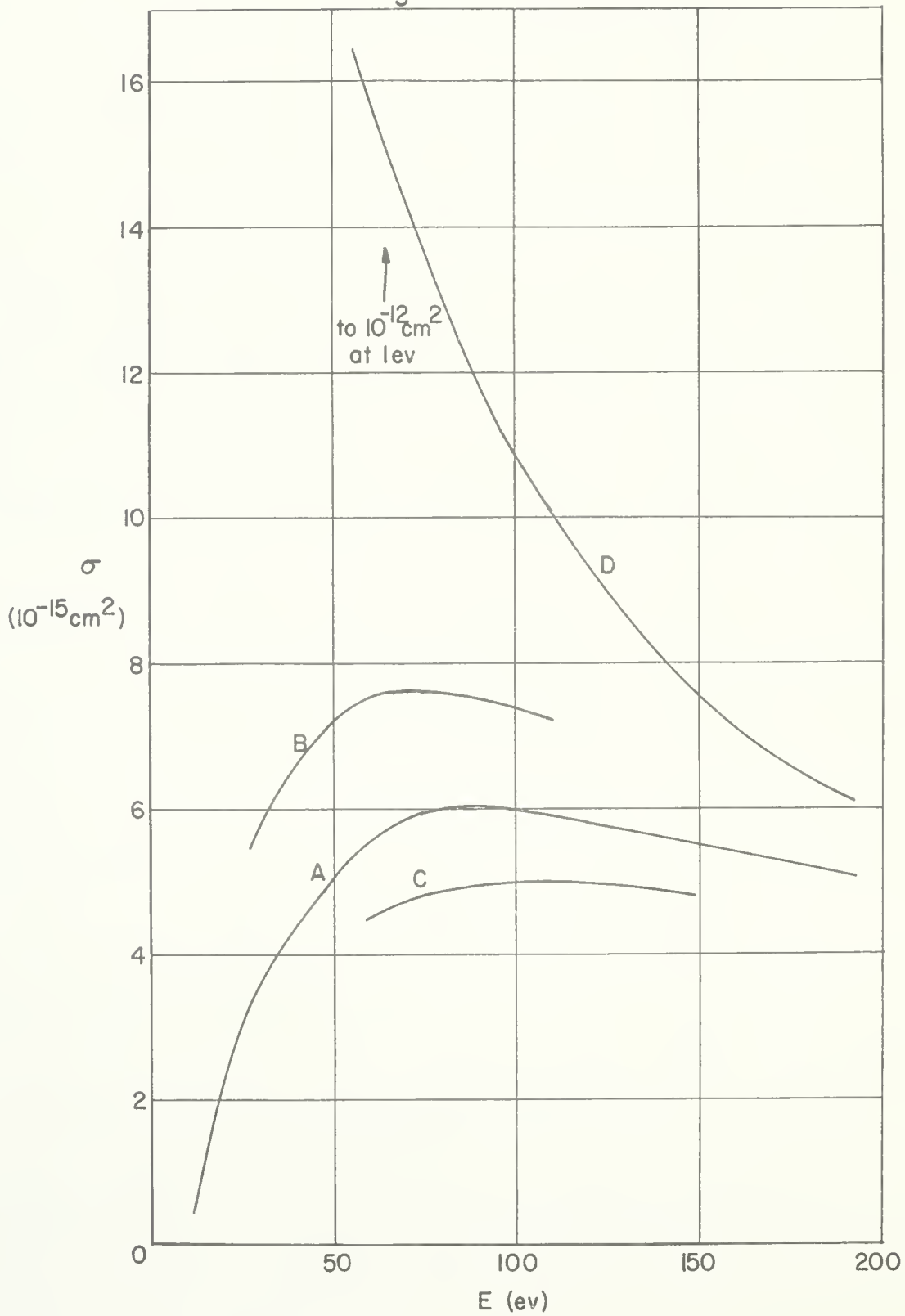


Figure 8

2.33 Low energy cross section

The low energy dependence of the inelastic cross section on energy is of some interest in the present calculation. It is in this region that the s-wave approximation may give reasonable results. Although it is known that this approximation will not do for a problem in inelastic scattering because of the importance of the higher phases, many theoretical calculations have been done for the case $\ell = 0$ since it is possible to handle it analytically for some simple forms of the intermolecular potential. We shall compare one calculation at a very low energy (initial energy at the threshold, 0.54 ev) with previous theoretical calculations in the s-wave approximation.

Zener^[9] considered the potential

$$(70) \quad V = D \left[e^{-2a(r-b)} - 2e^{-a(r-b)} \right] .$$

This potential has a minimum of $-D$ at $r = b$. It is a slight modification of the Morse potential used in the present work. Zener uses semi-classical methods to find the transition probability for a head-on collision with $\ell = 0$ since there are not available analytic continuous spectrum solutions to the radial equation for the potential (70). The result is

$$(71) \quad P_{nm} = \frac{8\pi^4}{a^2 h} \frac{M_C(M_B + M_C)M_A^2}{M_B(M_A + M_B + M_C)^2} \left(n + \frac{1}{2} \pm \frac{1}{2}\right) \nu \frac{\cosh^2(q_n - q_m)(\eta - \pi)}{\sinh^2 \pi(q_n - q_m)}$$

where

$$(72) \quad \cos \eta = \left(1 + \frac{E^*}{D}\right)^{-1/2} \quad E^* = \frac{1}{2} M^* \bar{v}^2 \quad \bar{v} = \frac{1}{2} (v_n + v_m) \\ q_n = M^* v_n / \hbar a ; \quad q_m = M^* v_m / \hbar a ; \quad M^* = M_A(M_B + M_C) / M_A + M_B + M_C .$$

In the present work

$$M_A = 2M_H ; \quad M_B = M_C = M_H ; \quad q_n = k_n / a ; \quad q_m = k_m / a ; \quad M^* = M_H = M_e .$$

Also, $n = 0$, and we must take the positive sign in (71). Then

$$(73) \quad p_{fo} = \frac{\pi^2}{2a^2} \left(\frac{2M_H \Delta E}{\hbar^2} \right) \frac{\cosh^2 \frac{1}{a} (k_o - k_f)(\eta - \pi)}{\sinh^2 \frac{\pi}{a} (k_o - k_f)} .$$

It is easily shown that this formula gives an incorrect value for the inelastic cross section when the energy is very large. When $k \rightarrow \infty$, $k_o \rightarrow k_f = k$, and $\eta \rightarrow \frac{\pi}{2}$. Also, since $k_o^2 - \eta^2 = k_f^2$, where η^2 represents the energy difference $2M_H \Delta E / \hbar^2$ between the ground and first excited vibrational states,

$$(k_o - k_f)(k_o + k_f) = \eta^2$$

$$k_o - k_f \rightarrow \eta^2 / 2k .$$

Hence

$$p_{fo} \rightarrow \text{const.} \cosh^2 A/k / \sinh^2 2A/k$$

where

$$A = \frac{1}{2} \pi \eta^2 / a .$$

For k very large, $\cosh^2 A/k \rightarrow \cosh^2 0 = 1$; $\sinh^2 2A/k$ approaches $(2A/k)^2$. Then

$$(74) \quad p_{fo} \rightarrow \frac{k^2}{4A^2}$$

for k very large.

Since the partial cross section is just $\sigma_\ell = (2\ell + 1)\pi / k_o k_f p_{fo}$, (74) gives a result for the cross section which is independent of energy. It is known, however, that the cross section must decrease as $(E)^{-1/2}$ for large energy.

At very low energies near the threshold, however, we may expect (73) to be a good approximation. We have calculated the inelastic scattering cross section on the Univac at the threshold energy, $E_o = .54$ ev, and with a final energy $E_f = 7 \cdot 10^{-5}$ ev. The same cross section was computed from (73). The results are

shown below.

	σ (cm ²)
Univac	$1.26 \cdot 10^{-26}$
Zener	$1.31 \cdot 10^{-25}$

Even at this very low energy the $\ell = 0$ approximation gives a result that is too large by a factor of 10.

3. Sensitivity of the cross section to variations of the potentials

We now examine the dependence of the inelastic cross section on the parameters of the unperturbed and perturbation potentials. Since the intermolecular potential is not known too precisely for most systems of interest, it is important to know just how the inelastic cross section varies when the potentials undergo small changes. The potential of the H_2-H_2 system used in Section 2 has three adjustable parameters for which values have been chosen to fit the best available data for the H_2-H_2 interaction. Since these data are uncertain, especially in the important region where the potential is steeply repulsive, it represents at best only an approximation to the actual potential between two H_2 molecules. We shall vary two of the parameters in this potential in a systematic way to determine just how sensitive the inelastic cross section is to small changes of these parameters.

There are two distinct types of variation to be considered. First, with a fixed unperturbed potential $V_e^0(r, \rho_0)$ we can vary the parameters in the perturbation potential. Since the perturbation potential is derived in an approximate fashion from the unperturbed potential, a knowledge of the variation of the inelastic cross section with small changes in the perturbation potential is necessary. From it we can see how accurately the perturbation potential must be known in order to obtain a given accuracy in the inelastic cross section.

Second, we can vary the parameters in the unperturbed potential $V_e^0(r, \rho_0)$. We are particularly interested here in the sensitivity of the cross section to variations in the steepness of the repulsive portion of the potential.

3.1 Sensitivity to the perturbation potential

The perturbation potential is given by

$$(75) \quad V'(\vec{r}; \vec{\rho}_0; \vec{\rho} - \vec{\rho}_0) = (\vec{\rho} - \vec{\rho}_0) \left(\frac{dV_e^0}{d\rho} \right)_{\rho=\rho_0}.$$

From Section 2, (26) and (29), the potentials are

$$(76) \quad V_e^0(\vec{r}, \vec{\rho}_0) = U_0 \left[e^{-2a(r-d)} - e^{-a(r-d)} \right]$$

$$(77) \quad V'(\vec{r}; \vec{\rho}_0; \vec{\rho} - \vec{\rho}_0) = U' a(\rho - \rho_0) \left[e^{-2a(r-z)} - e^{-a(r-z)} \right]$$

$$U_0 = 4.18 \cdot 10^{-4} \cdot e^2/a_0; \quad U' a(\rho - \rho_0)_{01} = 5.86 \cdot 10^{-6} e^2/a_0; \quad a = .916 a_0^{-1}$$

$$z = 6.87 a_0 \quad d = 5.67 a_0.$$

The wave functions calculated in Section 2 are used here, but the parameters a and d are now varied about the 'base' values of (77). The cross section as a function of energy is calculated for each new value of a and d .

The results of varying the steepness parameter a are shown in Figure 9. Two values of a roughly 5% greater and smaller than the base value of $.916 a_0^{-1}$ were chosen. We have also shown the result previously obtained in Section 2 using the potentials (76) and (77). We see that the cross section is a very sensitive function of the parameter a . A change of roughly 5% causes a variation in the cross section by a factor of about 2.5. This marked sensitivity to the value of the parameter a is to be expected from the following considerations.

Referring to Figure 3 in Section 2 we see that the turning point of the classical motion for the initial and final states at typical values of the energy

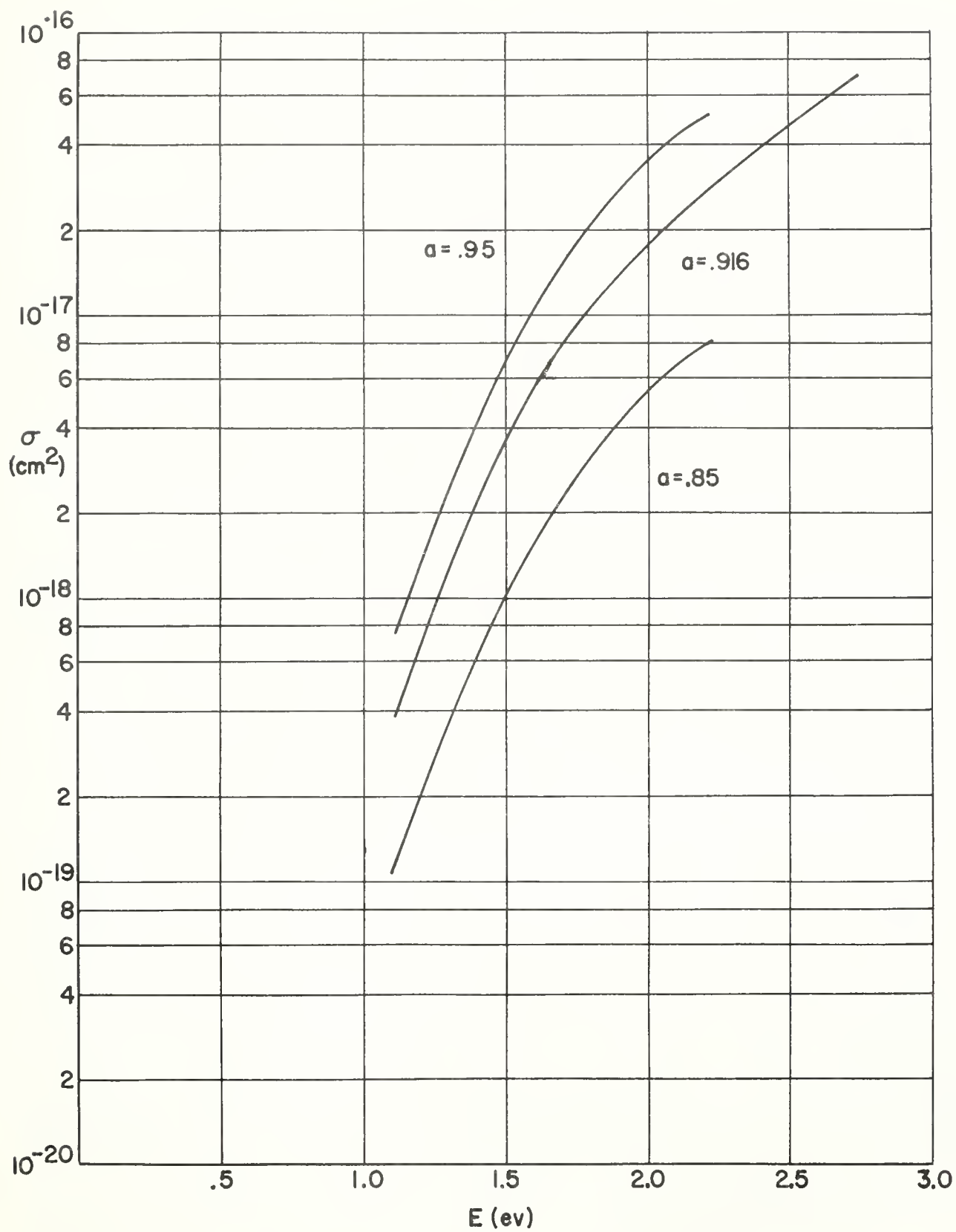


Figure 9

occur in a region where the perturbation potential is a very sharply varying function of r . The inelastic cross section is a function of the integral

$$\int_0^{\infty} \Psi_0(r) V'(r) \Psi_f(r) r^2 dr .$$

In the region near the turning points of the classical motion the product $\Psi_0(r) \Psi_f(r)$ is a quickly varying function of distance. Now the most important contribution to the integral comes from the first peak in the integrand and this first peak occurs near the turning points. (This can be seen approximately from the WKB representation for $\Psi_0(r)$ and $\Psi_f(r)$.) Since the perturbation potential is also a steep function of r near this first peak, it is clear why the inelastic cross section depends critically on the value of the perturbation potential in the region $0 < r < r_0$ (where r_0 is the value for which V' is zero). The perturbation potential in this region is in turn a very sensitive function of the parameter a , as can be seen from (77). Consequently the variation of the cross section with changes in a is very marked.

From the form of the perturbation potential, (26), it is clear that a change in the parameter d will produce essentially the same effect as changing the parameter $\underline{a}$. Changing the parameter d moves the whole perturbation potential bodily along the r -axis. In the region $0 < r < r_0$, which is the significant region in this problem, this is equivalent to multiplying the potential by a constant. However, the effect on the perturbation potential of changing the parameter $\underline{a}$ is the same, at least in the region of interest. Hence we may expect quite similar results for a change in d as those just described for changes in $\underline{a}$. For this reason, we did not carry out the calculations for variation of the parameter d .

3.2 Sensitivity to the unperturbed potential

We consider now the variation of the inelastic cross section with changes in the parameters of the unperturbed potential. It is evident that variations of the unperturbed potential will produce a variation in phase shift of the radial functions. These variations in the phase shift of the initial and final radial functions will cause changes in the cross section for the same reasons discussed in § 3.1. The first peak in the product $\Psi_0(r)\Psi_f(r)$ will be displaced along the r -axis because of the phase shift. Since the perturbation potential is very quickly varying in this region, the cross section will vary sharply with the variation in the phase shift.

We proceed to examine this effect in two stages. First, we calculate the variation of the cross section with phase shift in the radial functions. That is, we deliberately insert a phase factor δ in the expression for the transition matrix element V'_{f0} (Section 2, (51)):

$$(78) \quad V'_{f0} = \int \Psi_f(r \pm \delta) V'(r) \Psi_0(r) r^2 dr$$

and calculate the cross section as a function of δ . Second, we vary the parameters a and d in (76) and observe the change in δ and consequently in the cross section.

A first attempt at this program was made with the exp-six potential (Section 1, (8)):

$$(79) \quad V = \frac{\epsilon}{1 - \frac{6}{a}} \left[\frac{6}{a} \exp \left[a \left(1 - \frac{r}{r_m} \right) \right] - \left(\frac{r_m}{r} \right)^6 \right] .$$

This potential form is of interest because it has been widely used in recent years with moderate success for calculating transport coefficients and other equilibrium properties of gases. It has a spurious maximum at a small value of r of the order $2 - 2.5 a_0$. This is of no consequence in calculating the equilibrium properties of gases since they depend on the behavior of the potential near $V = 0$.

Values of ε , α and r_m were chosen so that (79) fits the available data on H_2-H_2 . The radial functions calculated with this potential agreed very closely with those calculated from the Morse potential, (77). For this Morse potential the transition probability is a monotonic decreasing function of ℓ . The transition probability for the exp-six potential (79), however, showed a wrong functional dependence on the angular momentum ℓ . It increased from some value at $\ell = 0$ to a maximum, and then decreased. Since the radial functions and unperturbed potentials were essentially the same for both the Morse and exp-six potentials, we could expect the transition probability to be the same function of ℓ for both potentials.

This behavior is easily accounted for by the spurious maximum in (79). Since the perturbation potential is derived from the unperturbed potential it too exhibits a maximum at $r \sim 2 - 2.5 a_0$. This, however, is a serious defect in the perturbation potential because of the relatively high energies we must consider. At these high energies the turning points of the classical motion for small angular momentum are near this spurious maximum in the perturbation potential. Consequently the first and most important peak in the integrand of the transition probability occurs in a region where the perturbation potential is too small. At higher values of angular momentum the turning points move out to greater values of r where the perturbation potential is larger, and behave correctly as a function of r . This accounts for the observed (incorrect) maximum in the dependence of the transition probability on ℓ .

For this reason the exp-six potential is of no use for calculating inelastic cross sections where the value of the perturbation potential at small r is important. Although this latter behavior is of no consequence in the calculation of equilibrium properties of gases, it is of the utmost importance in the calculation of inelastic scattering cross sections.

The exp-six potential was therefore abandoned and the Morse potential (76) used. The dependence of the cross section on the phase shift δ in (78) is shown in Figures 10 and 11. Two representative values of energy are shown, and two values of the angular momentum at each energy. These curves make clear that we have to integrate the radial equation very accurately in order to obtain the correct value of the cross section. An inaccuracy of just 1° in the phase shift of the final radial function can cause an error of as much as 10% in the calculated cross section.

Finally, we have taken two different values of the parameters a and d in (76) and calculated the cross section as a function of energy for each of these values. These results are shown in Figures 12 and 13. The cross section for the base potential (76) is shown for comparison. The variation in the phase shift of the radial functions with these changes in the parameters is of the order of 2 - 3 radians. This accounts for the large changes in the cross section with relatively small changes in the parameters.

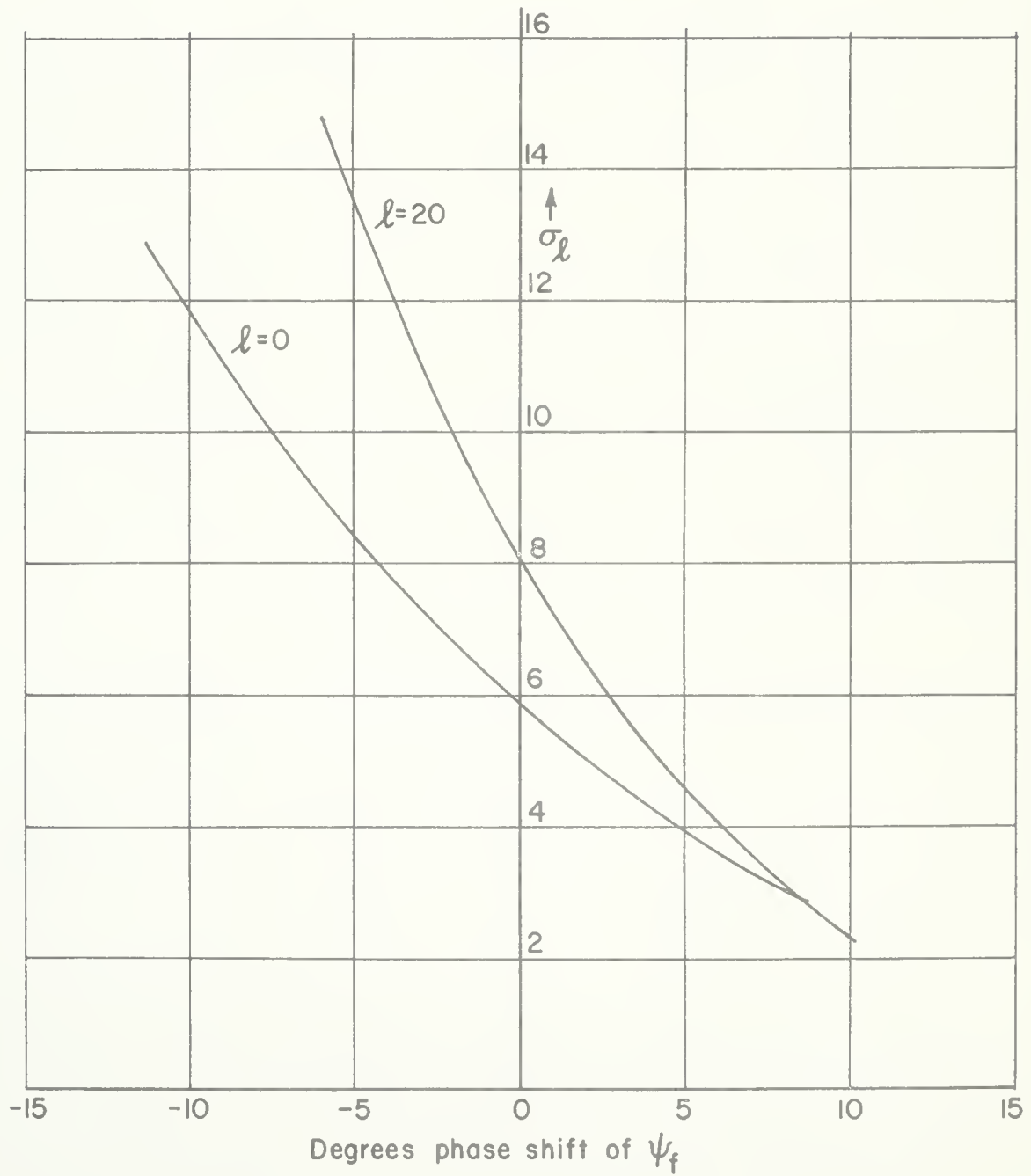
It is seen by comparing Figures 12 and 13 with Figure 9 that, as one would expect, the inelastic cross section is more sensitive to variations of the parameters in the perturbation potential than to the same variations in the unperturbed potential. A change in the steepness parameter a of about 5% in the perturbation potential produces the same effect as a change of about 10% in a in the unperturbed potential.

3.3 Summary

We have seen that the calculation of the inelastic scattering cross section requires the solution of the radial wave equation for very many values of the angular momentum l . This requirement is related to the large wave number k (or small de Broglie wavelength) of the system. In general, values of angular momentum up to

Inelastic cross-section as a function of phase
shift in final radial function.

(σ_l in arbitrary units)

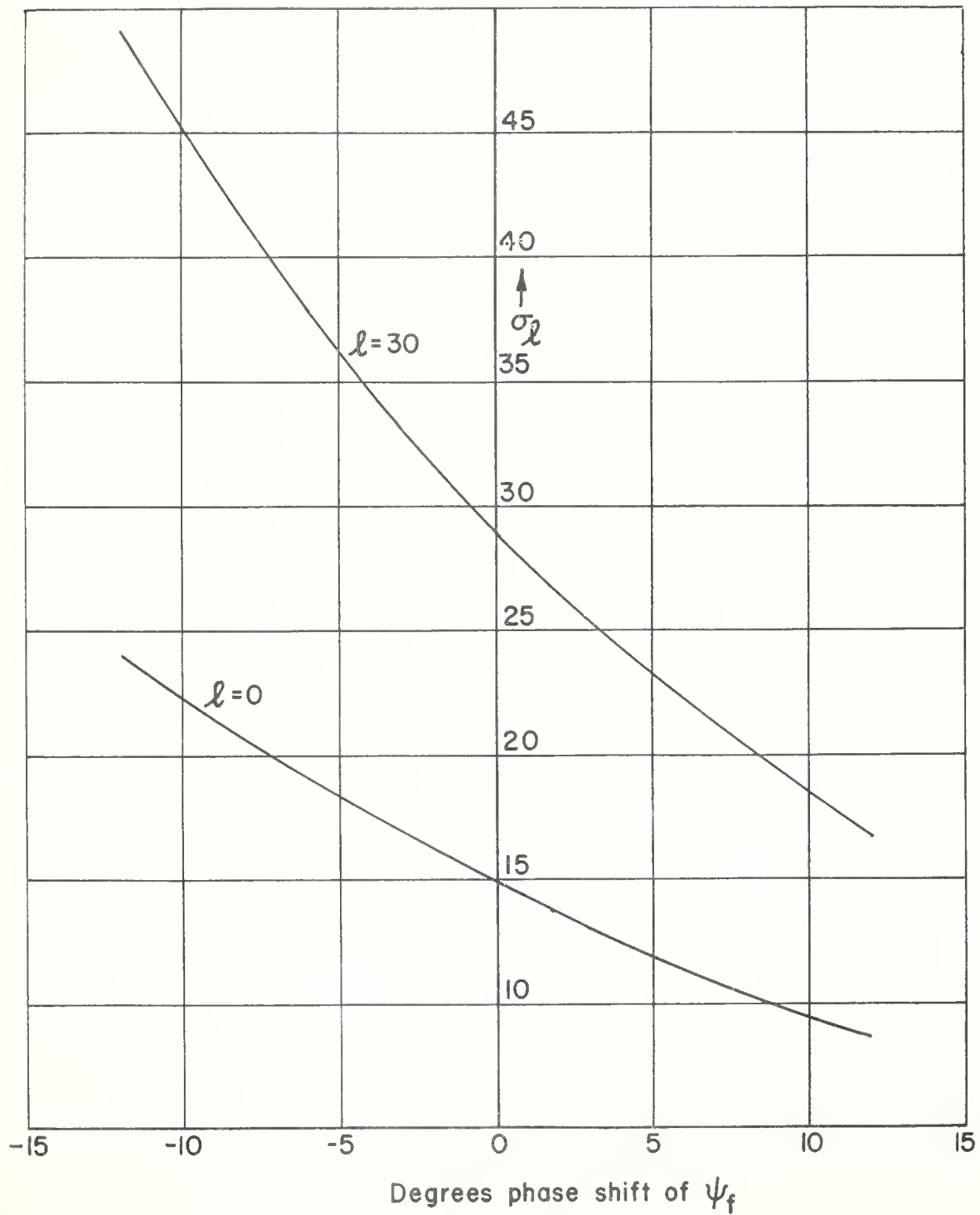


$E_0 = 1.1 \text{ ev}$
 $E_f = .56 \text{ ev}$

Figure 10

Inelastic cross-section as a function of phase
shift in final radial function.

(σ_l in arbitrary units)



$E_o = 2.2 \text{ ev}$

$E_f = 1.65 \text{ ev}$

Figure 11

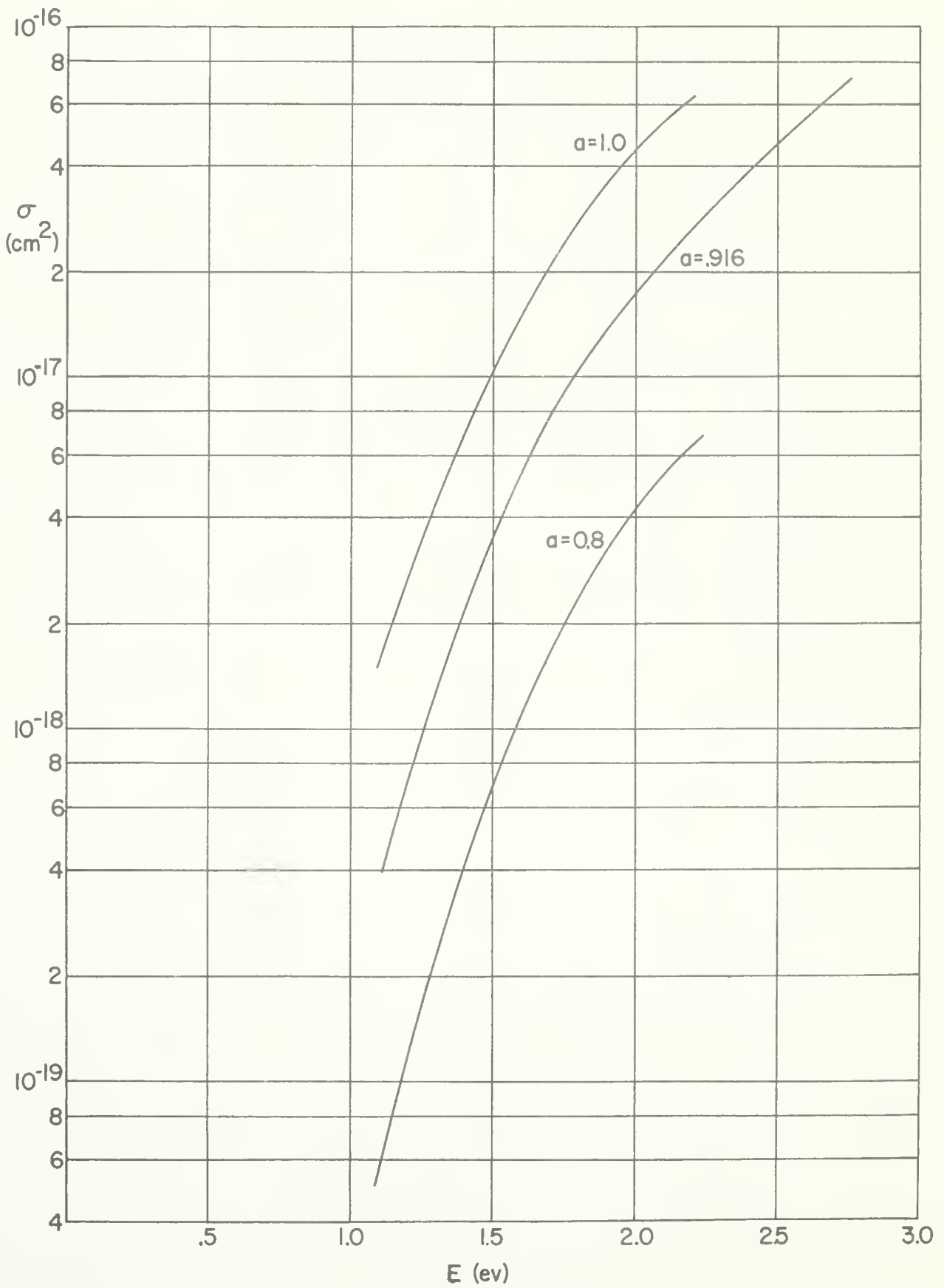


Figure 12

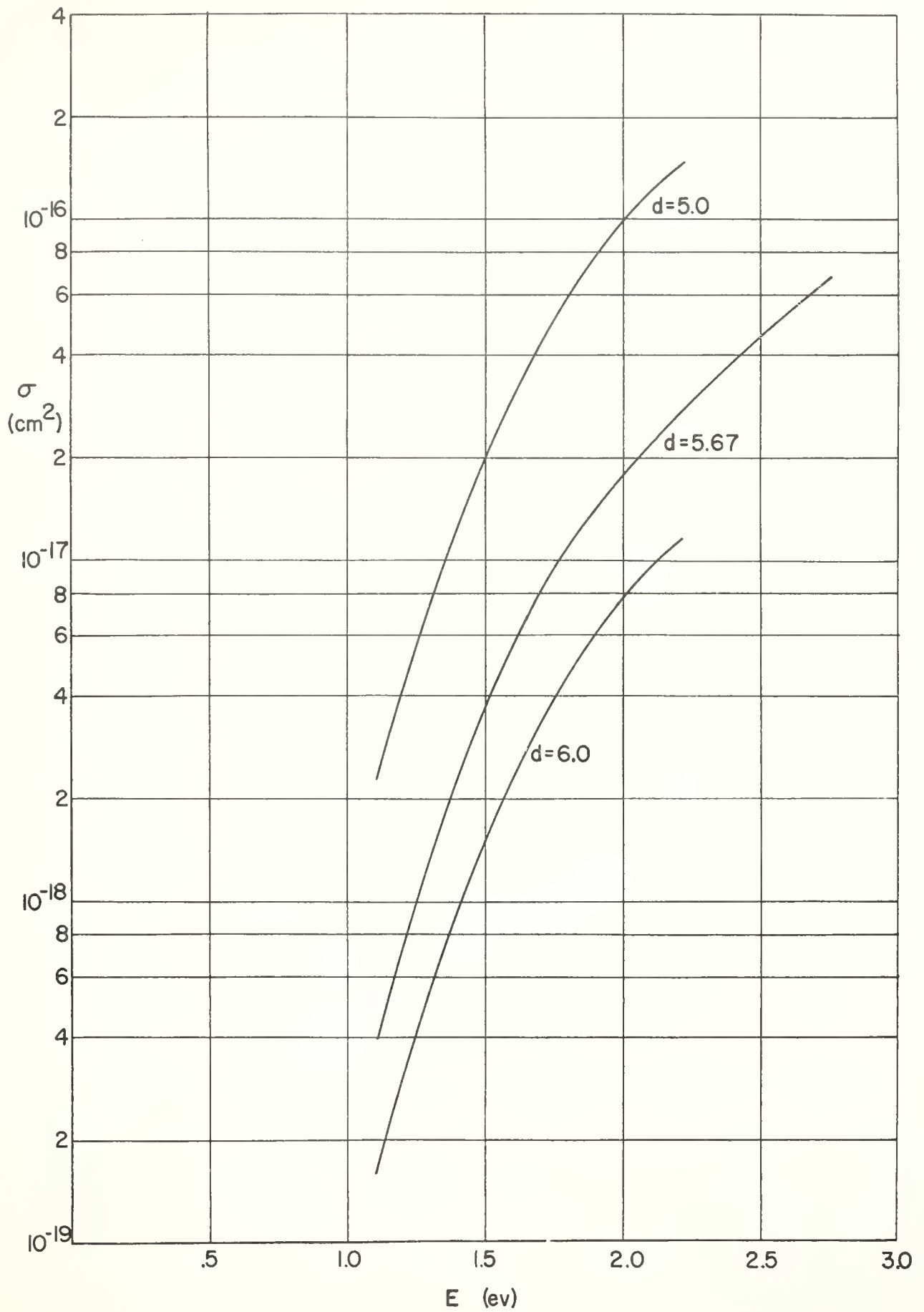


Figure 13

about kd where d is the range of the potential, must be considered. The radial equation can not generally be solved in closed form for all l except for the simplest and usually physically unrealistic potentials. Thus one is forced to do laborious computations. This presents no special difficulty in principle.

An analytic solution to the radial equation is available for the s-wave, $l = 0$, if the potential is not too complicated. This solution is the one that has been used until recently for molecular scattering problems. Zener and Devonshire have given the transition probability for the case $l = 0$ with a Morse potential. We have compared the present results with those of Zener in Section 2, § 2.3 at one very low energy ($E_f \sim 7.10^{-5}$ ev). It would be of interest to extend that calculation and compare the results over a larger range of final energies.

We have shown that an accurate calculation of the inelastic scattering cross section requires a most precise knowledge of the details of the interaction of the molecular system. The value of the inelastic cross section is much more sensitive to the details of the perturbation potential than to the unperturbed potential. This sensitivity of the inelastic cross section to the parameters of the potentials is due to the small de Broglie wavelength of the system. Because of the large reduced masses, the wavelength is very much smaller than the range of the potentials at the energies of interest (0.5 - 2 ev). Consequently the transition probability depends critically on the potentials.

The difficulty with the sensitivity of the inelastic cross section to the precise shape of the perturbation potential is not easily resolved. The perturbation potential is not well defined and can be obtained from an expansion of the unperturbed potential only if the molecules do not approach too closely. Inasmuch as a perturbation scheme is absolutely necessary for this many body problem, it is

clear that more work must be done to find the correct correlation of the internal and external motions of the molecules.

We have also seen in Section 1 that the details of the unperturbed potential for most molecular systems of interest are not known with any certainty. Most of the work on the empirical fitting of a potential form to experimental data has concentrated on the region near $V = 0$. However, no work has yet been done that gives the repulsive wall of the potential accurately. It is just this part of the potential that is needed for the calculation of an inelastic scattering cross section. Furthermore, since the potential is not known accurately in this region, the present calculations can be believed only to within an order of magnitude. The relative variation of the cross section with the change in the potentials is correct; however, the actual values for the cross section are not accurate.

Here we note that the calculation of the inelastic scattering cross section can itself be used to discover the form of the intermolecular potential in the region from $r = 0$ to the zero of the potential. Since the value of the cross section is acutely sensitive to the precise shape of the potential in this region, one can hope to fit data on inelastic scattering very precisely by adjusting the parameters of the potential. Unfortunately, very scant data are available on molecular scattering, whether elastic or inelastic. Such a program must await the availability of experimental molecular scattering data.

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